The pelleting of micro-fine agricultural lime to treat soil acidity, using sodium alginate, lignosulphonate, and bentonite as binders

by

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Thesis presented in partial fulfilment of the requirements for the degree of Master of Engineering (Chemical Engineering) in the Faculty of Engineering at Stellenbosch University

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March 2021

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Abstract

Limestone is often used to ameliorate soil acidity, as the release of carbonate ions neutralises acids in the soil. Agglomerated micro-fine limestone is an attractive alternative to powdered limestone for use in agriculture, mitigating product losses as a result of unfavourable weather conditions during and after conventional top-dress application. Binders, specifically sodium alginate, lignosulphonate and bentonite, were investigated in the agglomeration of micro-fine limestone. The effect that binder concentration had on agglomerate strength was investigated to determine whether the agglomerates were durable enough to withstand typical transport and handling processes.

Agglomerates were produced in an inclined disc agglomerator, set to 45°. The significance of rotational speed, liquid addition, and binder concentration were assessed using CCD analyses, with the yield of agglomerates of 2-5.6 mm in diameter, as the response variable. Speed of rotation was insignificant in the 20-55 rpm range and was set to 37.5 rpm. The volumes of liquid added proved significant in maximising the yield, with sodium alginate, lignosulphonate, and bentonite requiring 20 mℓ, 18 mℓ, and 22 mℓ of liquid per ≈100 g of powdered constituents, respectively.

To compare the effect that the binder concentration had on their physical properties, strength tests were carried out on agglomerates at concentrations of 1-7 g sodium alginate, 7.2-14.4 g lignosulphonate and 10-70 g bentonite, per kilogram. The results showed that sodium alginate performed significantly better in resisting breakage due to impact and compression. At significant concentrations for each binder type, they all produced agglomerates that performed acceptably in resisting abrasive wear. With the ability to absorb water, the agglomerates of bentonite included at > 40 g/kg resisted disintegration for longer than the other agglomerate types, when saturated in water. However, agglomerates containing sodium alginate and bentonite at 4 or 5 g/kg and 70 g/kg respectively, proved strong enough to withstand all stresses that may arise during transportation, storage and handling.

Specific to South African soil, the Eksteen method was used to determine the amount of limestone required to ameliorate soil acidity in the soil used in this research. Agglomerates containing sodium alginate at 4 and 5 g/kg, lignosulphonate at 14.4 g/kg, and bentonite at 40 and 70 g/kg were placed on the surface of 25 cm deep soil columns, in masses corresponding to the limestone requirement

of 0.01114 g/cm^3. The soil columns were exposed to a 14-week rainfall simulation, thereafter the movement of the limestone through the soil columns was investigated using XRF analysis of soil samples from different depths. These results, along with pH and electrical conductivity tests, showed that the limestone did not successfully penetrate or ameliorate soil acidity below 2.5 cm of the soil columns.

An inclined disc agglomerator was therefore successfully designed, manufactured, and commissioned for the agglomeration of limestone. This research successfully demonstrated that sodium alginate and bentonite are feasible binders for limestone, producing agglomerates with physical properties appropriate for commercial use. It was also demonstrated that the agglomerates would disintegrate when exposed to natural weathering, but would require significantly more time to ameliorate soil acidity at depths deeper than the surface.

Opsomming

Kalkklip word gereeld gebruik om grondsuurheid te verbeter, omdat die vrylating van karbonaatione sure in die grond neutraliseer. Geaglomereerde mikrofyn kalkklip is 'n aanloklike alternatief vir gepoeierde kalkklip vir gebruik in landbou, waar produkverlies as gevolg van ongunstige weerkondisies gedurende en na konvensionele bobemesting, verminder word. Verbinders, spesifiek natriumalginaat, lignosulfonaat, en bentoniet, is ondersoek in die agglomerasie van mikrofyn kalkklip. Die effek wat verbinderkonsentrasie op agglomeraatkrag gehad het, is ondersoek om te bepaal of die agglomerate sterk genoeg was om tipiese vervoer- en hanteringsprosesse te kan weerstaan.

Agglomerate is geproduseer in 'n skuins skyf agglomerator, op 45° gestel. Die beduidendheid van rotasiespoed, vloeistof byvoeging en verbinderkonsentrasie is geassesseer deur CCD-analise te gebruik, met die opbrengs van agglomerate van 2-5.6 mm in deursnit as die responsveranderlike. Spoed van rotasie was onbeduidend in die 20-50 rpm bestek en is gestel na 37.5 rpm. Die volume vloeistof bygevoeg was beduidend om die opbrengs te maksimeer, met natriumalginaat, lignosulfonaat en bentoniet wat 20 mℓ, 18 mℓ en 22 mℓ van vloeistof per $\approx$ 100 g gepoeierde bestanddele, onderskeidelik, vereis het.

Om die effek wat die verbinderkonsentrasie op hul fisiese eienskappe het te vergelyk, is kragtoetse uitgevoer op agglomerate by konsentrasie van 1-7 g natriumalginaat, 7.2-14.4 g lignosulfonaat en 10-70 g bentoniet, per kilogram. Die resultate het getoon dat natriumalginaat beduidend beter presteer het om afbreking te weerstaan as gevolg van impak en kompressie. By beduidende konsentrasie vir elke tipe verbinder, het hul almal agglomerate geproduseer wat aanvaarbaar presteer het om afskurende verwering te weerstaan. Met die vermoë om water te absorbeer, het die agglomerate wat bentoniet ingesluit het by > 40 g/kg disintegrasie vir langer as die ander agglomerate weerstaan, wanneer in water deurweek is. Agglomerate wat natriumalginaat en bentoniet by 4 en 5 g/kg en 70 g/kg, onderskeidelik, bevat het, was sterk genoeg om alle spannings wat kon voorkom gedurende vervoer, bewaring en hantering, te weerstaan.

Spesifiek tot Suid-Afrikaanse grond, was die Eksteenmetode gebruik om die hoeveelheid kalkklip te bepaal wat benodig word om grondsuurheid in die grond gebruik in hierdie navorsing, te verbeter.

Agglomerate wat natriumalginaat by 4 en 5 g/kg, lignosulfonaat by 14.4 g/kg, en bentoniet by 40 en 70 g/kg bevat, was op die oppervlak geplaas van 25 cm-diep grondkolomme, in gewigte wat met die kalkklip vereistes van 0.01114 g/cm^3 ooreenstem. Die grondkolomme is aan ’n 14-week reënval simulasie blootgestel, en die beweging van die kalkklip deur die grondkolomme is daarna ondersoek deur XRF-analise van grondsteekproewe van verskillende dieptes te gebruik. Die resultate, saam met pH- en elektriese geleidingsvermoÃ«toetse, het getoon dat die kalkklip nie suksesvol kon penetreer of grondsuurheid onder 2.5 cm van die grondkolomme kon verbeter nie.

’n Skuins skyf agglomerator is daarom suksesvol ontwerp, vervaardig en in gebruik geneem vir die agglomerasie van kalkklip. Hierdie navorsing het suksesvol gedemonstreer dat natriumalginaat en bentoniet uitvoerbare verbinders vir kalkklip is, wat agglomerate met fisiese eienskappe gepas vir kommersiÃ«le gebruik, produseer. Dit is ook getoon dat die agglomerate sou disintegreer wanneer dit blootgestel word aan natuurlike verwering, maar beduidend meer tyd vereis om grondsuurheid by dieptes dieper as die oppervlak te versag.

Articles arising from this work

An article titled "The effect of sodium alginate, lignosulfonate and bentonite binders on agglomeration performance and mechanical strength of micro-fine agricultural lime pellets" has been ACCEPTED for publication and has been published in *Particulate Science and Technology Journal* hosted by the Taylor & Francis Group.
It is available at: `http://dx.doi.org/10.1080/02726351.2020.1833387`

A draft article titled "The effect that surface applied sodium alginate-, lignosulphonate-, and bentonite-limestone agglomerates have on soil acidity" has been written and is due for comment by the supervisors of this research.

Acknowledgements

Over the past two years I have received a great deal of support, patience and assistance. Much of that support came from my two excellent supervisors, Dr Neill Goosen and Dr Robbie Pott. Thank you for welcoming me into the Process Engineering department with open arms, and for your patience and guidance throughout my time here. Thank you for providing opportunities for personal and professional growth and for always inspiring me with your passion for research.

Thank you to AECI (Nulandis) for providing me with the funding to begin and complete this chapter of my life. I will always be grateful for the opportunity that you have given me to further my studies, and work with these brilliant people.

Thank you to Heinrich and Alvin for providing me with the resources and support required to complete this research. Linda Mzayifani, you will be missed by many, thank you. Oom Jos and Oom Anton, it was always a joy to work with you and I appreciate all the interest, effort and support that I received over the last two years. I would also like to thank the Mechanical & Mechatronic Engineering department for equipping me with the skills and drive to take on and complete this research.

I am so thankful to have two of my friends, Storm Morison and Steven Sutton come into my life at the beginning of this journey. Storm, thank you for making my beverages a little hotter and my days a lot brighter. Steven, thank you for being so brilliant and for packing so much laughter into the last two years. I am so grateful to know the both of you.

Thank you to my family for providing me with unfailing support and continuous encouragement throughout all my years of study. Thank you for listening to and believing in me. Through my wild ideas and moments of panic, thank you.

Also, thank you to MS Teams for being there for all of us when the *open door policy* was not.

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List of Abbreviations

LR	Lime Requirement
B	Bentonite
CCD	Central Composite Design
CEC	Cation Exchange Capacity
EC	Electrical Conductivity
FM	Final Mass
IM	Initial Mass
LS	Lignosulphonate
Na-A	Sodium Alginate
NTI	Normalised Test Index
PVC	Polyvinyl Chloride Plastic
RO	Reverse Osmosis
RTC	Real-Time Clock
SMP	Shoemaker-McLean-Pratt
XRF	X-ray Flourescence

List of Symbols

$\$_L$	Cost per gram of limestone powder
$\$_X$	Cost per gram of binder
$\varnothing$	Agglomerate diameter
β	Inclination angle
A	Area
D	Disc/drum diameter
g	Gravitational acceleration
H	Titratable acidity
$L_{g/t}$	limestone mass in 1 ton of agglomerates
$\mathbf{M}_{carbonate}$	Molecular mass of the carbonate ($CaCO_3$ or $MgCO_3$)
$\mathbf{M}_{elemental}$	Molecular mass of the element (Ca or Mg)
$\mathbf{M}_{oxide}$	Molecular mass of the oxide (CaO or MgO)
N_c	Critical Speed
R_{XRF}	Result from XRF
R	Ratio required for Eksteen lime requirement
$X_{g/t}$	Mass of binder in 1 ton of agglomerates

Chapter 1

Introduction

"Although dirt-to-fork doesn't quite have the same ring as farm-to-fork, soil is critical to our culinary future." With these words Mary Beth Albright (2014) reminds us of the vital role good soil plays in successful and effective crop growth. Soil pH plays a critical role in the overall soil health, as it influences nutrient availability and absorption by crops. However, nitrogen required for the production of chlorophyll in plants is added to the soil in the form of ammonium (NH_4^+)-rich fertilisers. Fertilising can therefore be a procedure that disturbs a balanced soil pH through the addition of acidic hydrogen ions (H^+).

Once soil acidification takes place, other factors that contribute to the decline of soil quality are aggravated, putting further pressure onto the crop lands. These factors include the reduction of solubility of necessary ions, such as phosphorus. In severely acidic soil, toxic ions, such as aluminium, are leached out of the soil resulting in heavy metal contamination, which is especially detrimental when in the root zone. In this case, although the soil has the macro- and micro-nutrients it needs for efficient plant growth, aluminium toxicity hinders the growth of the roots and the plant as a whole.

With the majority of arable land classified as acidic, liming has been used for centuries to treat soil acidity, offsetting the acidifying effects of NH_4^+ containing fertilisers. Liming commonly makes use of agricultural lime or limestone ($CaCO_3$), where the carbonate ions neutralise the excess acidic H^+ ions in the soil, releasing water and carbon dioxide. The calcium component of limestone is a macro nutrient in plants, and therefore does not go to waste either.

In agriculture, limestone is traditionally applied to the soil in powdered form, with product losses and inconsistent dosing common when it is applied during unfavourable weather conditions. In order to mitigate these product losses, agglomerates of limestone could be introduced. Positive attributes related to the application of limestone in the form of agglomerates, compared to that of fine, powdered limestone, is the simplified transportation, handling and storage of the product before use, as well as

more accurate dosing of the soil due to fewer product losses. If the agglomerates are of a similar size to fertilisers and other soil amendment products, they could be applied using standard agricultural spreading equipment. It is however important to consider that when used on its own, limestone has a poor binding ability. Binders are therefore incorporated into the agglomerates to ensure that they remain intact during all processes prior to application.

In order to be industrially viable, agglomerates should be applied using conventional spreading equipment and should therefore have a diameter similar to that of common fertilisers, in the range of 2-6 mm. The agglomeration procedure was therefore investigated to determine the impact that speed of rotation, liquid addition and binder concentration had on the mass fraction of agglomerates in that size range (yield). Response surface methodology (central composite design) was used as the statistical tool of choice when constructing the experimental design to investigate these factors, with the yield as the response variable.

Sodium alginate, lignosulphonate and bentonite are binders that could be considered in the agglomeration of limestone. The binder incorporated into the agglomerates should result in an agglomerate that is both strong enough to withstand the stresses that may be present during transportation, storage and handling, but also economically viable for commercial use. Mechanical strength tests were carried out on the agglomerates to determine the effect that binder type and concentration thereof had on their strength.

With the use of fine limestone powder, large surface areas may allow the limestone to impact the soil pH more readily than more coarse limestone particles. With the surface area reduced due to the agglomeration of the limestone, the binders should allow the agglomerates to disintegrate over time in order for the limestone to have a similar effect on the soil as if it were applied in powdered form. Therefore, after application to the soil, the agglomerates should be exposed to rain or irrigation water, from which they should disintegrate. The disintegrated agglomerates result in fine limestone particles that have the potential to filter through the soil profile along with the applied water. This may give the limestone the opportunity to neutralise soil acidity at levels deeper than the top 5 cm of the soil profile, more importantly - the root zone.

This thesis investigates the use of sodium alginate, lignosulphonate, and bentonite in the agglomeration of micro-fine limestone used to ameliorate soil acidity in agricultural soils. It is structured as a series of 6 chapters. Chapter 2 is a review of the literature pertaining to the proposed topic. The literature review discusses soils and how pH imbalances are treated in the agricultural industry. Lime-

stone is discussed as a method of treating soil acidity, where agglomeration of limestone with the use binders is introduced. Previous studies regarding the movement of limestone through soil are also investigated so as to develop an understanding of the use of limestone to treat soil acidity. Chapter 3 gives the aims, objectives and scope of this thesis. The materials used and experimental methods that are followed in order to satisfy these aims are described in Chapter 4. Chapter 5 includes results of the experiments carried out and in-depth discussions thereof, with conclusions and recommendations presented in Chapter 6.

Chapter 2

Literature Review

2.1 Soils

Soil is a key component in agriculture that should support successful and effective crop growth, providing physical support, anchorage, a water reservoir, and mineral nutrients to crops (Coleman and Thomas, 1967). It is a well-structured eco-system that is formed over hundreds of years when organisms (such as humans, vegetation, and micro-organisms) and varying weather patterns interact with rocks and other forms of soil parent material (Campbell, 2017). Vegetation is the primary source of organic matter and is therefore a dominant factor in soil formation and has a major role in the nutrient cycling of the site. The parent material of soil generally originates from sediments and weathering material that remain atop the hard rock from which it forms (Food and Agriculture Organization of the United Nations, 2006). Approximately half the soil volume consists of pores of various sizes, where available water is typically adsorbed in the smaller pores, while the larger pores provide drainage as well as aeration to the soil. The water stored in the soil is known as the soil solution and is necessary for chemical processes to occur. These include mineral hydrolysis, decomposition of organic matter, removal of water-soluble material, and oxidation of sulphates. These processes all have an impact on the properties of the soil, one being soil pH (Campbell, 2017). The nature of the micro- and macropores, as well as the bulk density of the soil is a means to characterise the structure of the soil. This soil structure is dependent on the soil texture, organic matter, and agricultural practices, where along with climate and terrain, it is a deciding factor when determining the potential that a land has for agricultural use (Lambrechts and MacVicar, 2004; Chaplain et al., 2011).

The Western Cape region of South Africa has a Mediterranean-type climate characterised by its winter rainfall. The cold Benguela current present off the west coast has a stabilising effect on the air pressure, creating summer aridity in the region (Meadows, 2003). In South Africa, land use changes that have been brought on by urbanisation and agricultural developments have been especially prominent.

The Swartland region, is an agricultural district in the southwestern Cape of South Africa. Approximately 80% of rainfall in the Swartland region falls between the months of April and September, with an average annual rainfall of 450 mm (data obtained from the South African Weather Services). The region has been exposed to increasing agricultural development and human activity, where the most abundant natural vegetation (West Coast Renosterveld) only survives in less than 5% of its original range. The vast fields in the region now exhibit wheat as a dominant agricultural product, where very little of its original vegetation remains (Halpern and Meadows, 2013). The impacts of land use change extend further than lack of diversity in resident fauna and flora, but include accelerated soil erosion and deterioration as a result of intensive cultivation.

The increasing global population results in an increased need for arable land for agricultural use. The health of agricultural soil is under pressure due to various forces, including overuse as a result of decreasing availability of arable land, and degradation and erosion due to some current farming practices. Soil degradation that is caused by natural weathering should be managed with farming techniques to prevent loss of topsoil through the unobstructed flow of run-off water. If this is not managed, terrain deformation can occur, which could lead to flooding and severe destruction of once fertile land (Oldeman, 2000). The combination of natural and human impacts lead to soil erosion, acidification and soil depletion, influencing the soil quality throughout the soil depth, and ultimately the crop yield and quality (Jie et al., 2002).

A soil profile is made up of different main horizons, the O-, A- and B-horizons. The O-horizon is the top layer of the soil composed of organic material, such as dead plant matter and surface organisms. The A-horizon (topsoil) lies below this layer and is approximately 25 cm deep. It consists of organic material and is often soft and porous to hold enough air and water to sustain forms of life, such as seed germination, roots, worms, fungi, and bacteria. The B-horizon is referred to as the subsoil and lies below the topsoil. Although this layer generally has very little organic matter or humus, plant roots often penetrate through it. The soil quality and pH should therefore be maintained at levels deeper than the top soil to provide for a healthy environment for crop growth (Foth, 1990).

2.2 Soil acidity and alkalinity

Even in relatively stable soil systems, chemical degradation can occur when there is an insufficient balance between the crop yield and the input of organic matter or nutrients in the soil. This includes the rapid loss of topsoil as a result of natural vegetation being removed from a site, salinisation, and

acidification.

Salinisation is a form of chemical deterioration that commonly occurs in coastal regions, where saline ground water or sea water filters into the soil profile of the land and disturbs the salt content of the topsoil (Oldeman, 1992). Soil acidification is a form of chemical deterioration that occurs when an imbalance in the soil pH causes the soil to be too acidic to sustain healthy crop growth.

The soil pH is a measure of the hydronium (H_3O^+) ion (otherwise referred to as H^+) activity in the soil solution and is described as the negative logarithm of the mol/ℓ H^+ in the soil solution (Eckert and Sims, 1995; McCauley, Jones, and Jacobsen, 2003). Since H^+ is a cation, it will compete with other cations (Ca^{2+}, Mg^{2+}, K^+) in the soil profile to bond with available cation exchange sites on the surfaces of clay and organic matter in the soil. The cation exchange capacity (CEC) can be explained as the soils ability to retain nutrients, where a high CEC allows the soil to bind with more cations, such as Ca^{2+} and Mg^{2+}. When the soil binds to these buffering cations, it can resist changes in the soil pH as there would be little room for the soil to bind to H^+ ions (McCauley, Jones, and Jacobsen, 2003). Soil is considered to be alkaline when the pH of the soil is above pH 7 or there are more cations that are not H^+ attached to the cation exchange sites. This makes the soil less susceptible to leaching nutrient cations such as, Ca^{2+}, Mg^{2+} and K^+ (McCauley, Jones, and Jacobsen, 2003). Droughts or a drastic reduction in irrigation of a piece of land can also cause increased soil alkalinity as the drainage rates decrease, leading to the reduction of base cation, H^+, and Al^{3+} mobility - ultimately the retardation of acidification. Soil acidity is therefore common when rainfall or irrigation exceeds evaporation and transpiration (Kamprath and Smyth, 2005; Kopittke, Tietema, and Verstraten, 2012).

Soils are considered acidic when the soil horizons (especially at a depth of 0-25 cm) have a pH lower than 5.5, which is the case for more than 30% of the global land surface, accounting for approximately 50% of arable land (von Uexküll and Mutert, 1995; Sumner and Noble, 2003; Li et al., 2018). Along with soil erosion, acidification is one of the largest causes of low crop productivity. This is because acidified soil exacerbates the toxicity levels of potentially damaging ions in the soil, such as Al^{3+}, while reducing the availability of several essential elements, such as phosphorus (Li et al., 2018). Land management practises often make use of synthetic products, such as fertilisers, to add essential elements to the soil. However, the leaching of nitrates and the input of acidifying substances, such as these ammonium (NH_4^+)-based fertilisers are the leading causes of soil acidification (Tang and Rengel, 2003). Equation 2.1 shows how intensive agricultural practices, such as the application of NH_4^+-rich fertilisers, can release H^+ (acids) into the soil as part of the chemical reaction when NH_4^+

is converted into nitrate (Bolan, Curtin, and Adriano, 2005).

$$NH_4{}^+ + 2O_2 \rightarrow NO_3{}^- + H_2O + 2H^+ \tag{2.1}$$

Soil acidification can also occur due to the breakdown of soil biomass or decomposition of plant matter. Carbon dioxide and organic acids are produced during this process, where the excess carbon dioxide reacts with water in the soil to form carbonic acid which in turn releases H^+ (Campbell, 2017).

Acid rain can be another precursor to acidified soil, caused by the release of SO_2 and NO_2 into the atmosphere, mostly through the burning of fossil fuels. The SO_2 can dissolve in moisture in the atmosphere to form dilute sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4). This, along with nitrous and nitric acids that are formed in the same way from NO_2, forms the basis of acid rain (Kamprath and Smyth, 2005; Campbell, 2017). Acidic rain therefore adds additional H^+ to the soil, offsetting the pH balance of the soil (Sumner and Noble, 2003).

Soils that are kept at a near neutral or alkaline pH have exchangeable bases that are in dynamic equilibrium with the ions in the soil solution and balance the anions that are present on the soil colloids. The soil colloids are the finer fractions of the soil, generally considered to be the most chemically active portion of the soil due to their large surface area (Gavrilescu, 2014). When the soil is saturated, water soluble material is removed from between the colloids, including the dominant, free alkaline cations (Ca^{2+}, Mg^{2+}). These cations are replaced with acidic $H^+(aq)$ and $Al^{3+}(aq)$ ions, lowering the pH of the soil (Campbell, 2017). Again, acidic soil is therefore common in areas with high rainfall, due to the relative ease in which base cations leach from the soil (van der Berg, Hardie, and Raath, 2017).

When the soil pH drops to below 5.5, aluminosilicate clays and aluminium hydroxide minerals start to dissolve, allowing additional aluminium (Al^{3+}) to be released into the soil and exchange with other cations. Al^{3+} is considered to be one of the most toxic forms of aluminium for plant growth, providing a serious constraint to most crops due to aluminium toxicity. Hindered root growth is one of the main consequences of aluminium toxicity, where crops such as wheat experience a decrease in mitotic activity and disruption of regulatory signals at the root tips (Silva, 2012; Barth et al., 2018; Kamprath and Smyth, 2005). The crops may also experience oxidative stress due to aluminium toxicity, and ultimately soil acidity, when Al^{3+} bonds to the membranes of the crop leading to ridgification of the plant. High concentrations of aluminium ions in the soil solution invokes a rapid and irreversible

displacement of Ca^{2+} from the cell wall, allowing Al^{3+} to bond to the cell wall constituents. This leads to an alteration in the structure, functions, and properties of the cell walls, such as porosity, enzyme activity and extensibility - leading to further inhibition of root growth (Silva, 2012; Barth et al., 2018). The visible effects of aluminium toxicity include a reduction in the length of the crop root, causing the crop to suffer from underdevelopment and nutrient deficiency, as well as sensitivity to drought stress (Kamprath and Smyth, 2005).

No-till agriculture is a method of farming, where the soil is not turned during the planting of seeds or crops. It reduces the effect that tillage had on the labour costs, soil erosion and soil water evaporation. However, soils under continued no-till agricultural practices generally have stratified soil acidification due to soil amendments being placed on the surface and the subsequent lack of mixing (Barth et al., 2018). Soils of the same area will generally exhibit similar patterns, where surface acidification can occur due to the addition of NH_4^+-rich fertilisers and the decomposition of plant matter. In contrast though, the soil surface could have a higher pH than its underlying soil, due to surface liming. It is therefore important as part of soil management to test the soil pH at different depths and at least once every three years or twice per crop rotation (Crozier et al., 1999), where soils should be monitored and treated to have a pH that is suitable for the crop that it supports.

2.3 Management of soil pH

There are many approaches in attempting to modify or correct soil pH. These include addition of fertilisers, employing certain tillage practices, altering soil drainage, and applying nutrient amendments and agricultural lime (McCauley, Jones, and Jacobsen, 2003).

Alkaline and acidic soils are treated differently, as alkaline soils require the addition of H^+ ions, whereas acidic soil require the removal thereof. Most crops can survive in a more alkaline environment, rather than an environment that is too acidic than what they require. This is because of, amongst other factors, the heavy metal toxicity that becomes apparent with crops in acidic soil.

2.3.1 Alkaline soils

Alkaline soils are very common in semi-arid and arid climates. These soils are typically saturated with carbonates and are usually free draining due to their high porosity. Long-term use of ground water that is high in calcium, magnesium or carbonates can also be the cause of high soil alkalinity.

The solubility of phosphorus is limited by the abundance of calcium ions found in alkaline soils. Instead of soluble phosphorus, barely soluble calcium phosphate compounds are formed, depriving crops of a significant macro-nutrient (Lopez-Bucio et al., 2000).

Elemental sulphur (S^0) is commonly added to alkaline soil in order to lower the pH. The sulphur is oxidised by microbes in the soil to release sulphate (SO_4^{2-}) and H^+, lowering the pH of the soil (Slaton, Norman, and Gilmour, 2001). Often, ferrous sulphate ($FeSO_4$) and aluminium sulphate ($Al_2(SO_4)_3$) can be applied to soil in order to lower the pH. Although sulphates are added to the soil using these products, the acidic cations (Fe^{2+} and Al^{3+}) are the main contributors to the acidification (McCauley, Jones, and Jacobsen, 2003). Neutralisation reactions in the soil solution can be caused by the nitrification of organic nitrogen, producing inorganic acids that assist in the lowering of soil pH. A release of H^+ and Al^{3+} cations from the soil in response to additional inorganic acids is significantly related to the presence of nitrates, due to this nitrification (Kopittke, Tietema, and Verstraten, 2012).

As soil pH is described as the negative logarithm of H^+ ions, the addition of H^+ to the soil would be a logical means to lower the pH. Therefore, ammonium (NH_4^+)-based fertilisers, such as urea and ammonium phosphates, are an effective means to treat alkaline soils. Microbes in the soil oxidise the soil amendments and release the H^+ ions. Organic matter containing urea is also commonly used for this treatment, where the matter is mineralised to form organic and inorganic acids (McCauley, Jones, and Jacobsen, 2003). It may be difficult to successfully acidify soils, as other agricultural practices such as tillage or cultivation results in the removal of organic matter from the soil profile, causing a decrease in subsequent acid formation.

2.3.2 Acidic soils

Although slightly acidic, most crops grow well in soil with a pH of 5.5 - 6.5 and agricultural techniques are often used to keep the pH within this range. Soils of pH 5.5 or lower likely contain exchangeable Al^{3+} that may be at levels high enough to be toxic to crops. The increase in concentration of metallic ions, such as Al^{3+}, at a low pH is a result of the hydrolysis of insoluble oxides in which they occur, whereas soils of pH 4 or below are likely the result of oxidation of sulphur or sulphur-containing compounds (van Lierop, 1990).

Literature shows that an increase in soil pH and buffering against soil acidification can be achieved through liming. Through the application of limestone, cations in the soil are replaced by Ca^{2+} and small amounts of Mg^{2+}, reducing the solubility of heavy metals and the toxicity thereof (Bolan, Curtin,

and Adriano, 2005; Jovanovic et al., 2016; Campbell, 2017). Limestone powder has therefore been used extensively to overcome soil acidity problems.

As $CaCO_3$ slowly dissolves in water (Equation 2.2), the carbonate ions bond with two H^+ ions, forming undissociated carbonic acid (H_2CO_3), increasing the pH. This is because, carbonic acid dissociates into bicarbonate (HCO_3^-) and H^+. Equation 2.3 shows how dissociated carbonic acid forms H_2O and CO_2 when out of equilibrium, reducing the soil acidity caused by the free H^+ ions. The negative charges on the surfaces of the clay and humus particles in the soil attract these free H^+ and Al^{3+} ions. However, as the limestone solubilises, the increase in Ca^{2+} ions in the soil solution displace these cations, allowing the dissociated carbonic acid to further neutralise acidic ions in the soil profile (Campbell, 2017). Figure 2.1 shows this process.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightleftharpoons Ca^{2+}(aq) + 2\,HCO_3^-(aq) \tag{2.2}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons 2\,H_2O(l) + CO_2(g) \tag{2.3}$$

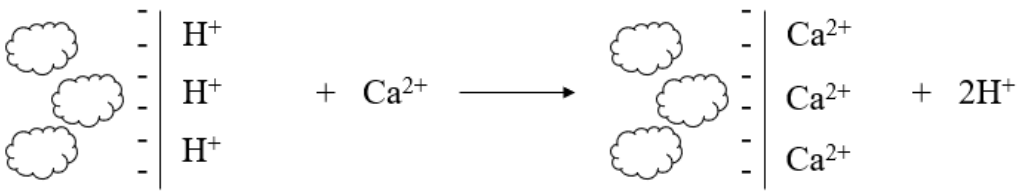


Figure 2.1: A representation of how the calcium ions added to the soil through the addition of limestone assist in the further removal of acidic H^+ ions from the soil colloids (cloud-like figures). Redrawn from Campbell (2017).

Limestone can also be substituted with alkaline stabilised bio-solids for the treatment of soil acidity, where the pathogens in the bio-solids are killed and the organic matter is stabilised through a combination of high pH, heat, and drying. Some of these limestone-replacement materials include, cement-kiln dust, coal fly ash and, wood ash (Bolan, Adriano, and Curtin, 2003). However, in combination with moisture, settled cement kiln dust can form crusts on the soil surface, as well as the crops that it comes into contact with, leading to a change in the physical properties of the soil and

stunted crop growth (Darley, 1966; Eugene Lamare and Singh, 2020). Coal fly ash is a waste material resulting from the combustion of coal-fired power stations. It is often overlooked as a limestone alternative due to the presumption of high levels of heavy metals and the uncertainty of its pH buffering capacity (Harper and Mbakwe, 2020). Wood ash has a calcium carbonate equivalent (CCE) of approximately 25 - 59%, whereas agricultural limestone has a CCE of approximately 90 - 95%. Therefore, 2 - 4 times more wood ash would be required to improve soil pH to the same level to that of limestone, making it unattractive for commercial use (Saunders, 2014).

2.4 Types and forms of limestone used in agriculture

Limestone is a sedimentary rock composed mainly of calcium carbonate, but may also contain skeletal fragments of marine organisms. It is believed to have formed through the extraction of calcium salts in early igneous rocks from weather erosion and corrosion by dissolved acids (Oates, 2005). The limestone is removed from mines where it is crushed to a different fineness depending on its use. It has been apparent for hundreds of years that the primary use of limestone in agriculture is to neutralise acidic soils, without adding one of the three major primary macro-nutrients (N^{3-}, P^{3-}, K^{+}) to the soil. It is therefore classified as a soil amendment product rather than a fertiliser.

The surfaces of the chemically active soil colloids are more accessible to fine particles of limestone, therefore the neutralising value of the limestone is dependent on its purity, particle size and chemical composition (Zimdahl, 2015). The chemical and physical properties of the limestone are dependent on the origin of the deposit and its impurities. Although it is generally white in colour with a musty or earthy smell, these impurities may cause this to vary slightly (Oates, 2005).

Agricultural lime is a ground limestone product that contains calcium or magnesium oxides, hydroxides or carbonates (Lukin and Epplin, 2003). Although limestone has the chemical formula $CaCO_3$, $MgCO_3$ is not seen as an impurity, but rather when there is 20-44% $MgCO_3$, the limestone is considered to be dolomitic, whereas with a high calcium content it is referred to as calcitic limestone (Oates, 2005; Jones and Mallarino, 2018). However, silica and alumina in the form of clay, silt and sand, can be considered impurities that are commonly found in limestone deposits.

The particle size of agricultural lime is a determining factor in the dissolution rate and its effectiveness in treating soil acidity. Finer limestone particles have an increased total surface area, allowing the limestone to react with a larger volume of soil (Jones and Mallarino, 2018). The finer particles will

however also dissolve more rapidly, where consequently the effect of the limestone is quickly removed from the soil as well. More coarse limestone particles will remain in the soil for longer periods of time, slowly neutralising the soil acidity. Soil is generally tightly packed, making it difficult for coarse limestone particles to move through the soil profile. The more coarse limestone particles will therefore rely on the solubility (although poor) of the limestone in rain or irrigation water to treat subsoil acidity, whereas fine limestone has the potential to filter through the soil particles to treat subsoil acidity.

Quicklime (CaO) is produced through the thermal decomposition of limestone. Where calcium carbonate is heated above 825°C, calcination occurs and liberates the carbon dioxide in $CaCO_3$, producing the quicklime (Zimdahl, 2015). Although this product has a higher neutralising value than that of agricultural lime, if not handled correctly it can damage crops and be dangerous to handle. When water is added to quicklime, hydrated limestone ($Ca(OH)_2$) is formed. This too is a quick reacting, powdery product that harbours the same dangers as that of quicklime and is therefore also unpleasant and inconvenient for commercial use (Zimdahl, 2015; Feeco International Organization, 2018).

Gypsum ($CaSO_4$) can also be used to assist with soil acidity, where it has been shown to be effective in alleviating subsoil acidity. Gypsum can be mined as a dihydrate ($CaSO_4 \cdot {}_2H_2O$), be collected as a by-product in the manufacture of phosphoric acid or from the flue gases in fossil fuel powered generators (Sumner, 1993). It does not have the ability to neutralise the soil as a result of a carbonate ion reacting with H^+ ions, but rather relies on the Ca^{2+} ion to decrease the saturation of the toxic Al^{3+} ions in the soil. The Al^{3+} is therefore replaced and leached from the soil, alleviating toxicity (Oates and Caldwell, 1985; Wang et al., 1999).

Although acidic topsoil is commonly treated with limestone, it takes time to have an effect on acidic subsoils. The downward movement of limestone is markedly slow, where Reeve and Sumner (1972) state that when saturated with de-ionised water, a soil profile heavily treated with surface-applied limestone, recorded Ca^{2+} at a maximum depth of 45 cm. However, gypsum showed results of Ca^{2+} moving rapidly through the soil profile. Gypsum that is applied to soils that are rich in variable charge components, such as aluminium and iron, results in a phenomenon commonly referred to as the "self-liming effect" proposed by Reeve and Sumner (1970). This occurs when the ${SO_4}^{2-}$ in the gypsum is adsorbed, substituting the OH^- in the soil. These OH^- ions then go on to neutralise acidic cations in the soil solution (Reeve and Sumner, 1972; Bolan, Adriano, and Curtin, 2003; Goulding, 2016). Although gypsum can be used in the amelioration of acidic soils, it has a neutralising value

of 12.4 compared to the 100 of limestone (Bolan, Adriano, and Curtin, 2003), making limestone approximately 8 times more effective.

Soil amendment products can be applied in many different forms, including as a powder, a pellet, or as a suspension in water. Limestone applied as a suspension in water (referred to as liquid limestone) is a method of liming with approximately 50% limestone, 50% water. It is a costly method of liming as both the water and the limestone are to be transported for application. Under-liming is also an expected consequence with this method of soil neutralisation due to the spread rate, where more frequent applications may be required as the liquid product reacts quicker than that of dry limestone (Feeco International Organization, 2018; Corriher-Olsen, 2019). The shorter reaction time can however be an advantage, along with the ability to apply the limestone uniformly over the crop land (Corriher-Olsen, 2019).

Another crushed limestone product is powdered limestone. This is a finely ground limestone that is quick reacting due to increased surface area. However, increased product losses due to dusting, make it difficult to effectively apply powdered limestone to the soil in unfavourable (windy) weather conditions. Pelleted limestone is when powdered limestone is used along with a binder to form a pellet (Jones and Mallarino, 2018). The pellets allow for relatively uniform application of the limestone when applied with standard spreaders. This makes application easier and more efficient when compared to that of powdered- or liquid-limestone, as it largely reduces product losses when applied in windy conditions. Decreased dusting of the product in comparison to powdered limestone, makes pelleted limestone more simple to transport and store, while also making it more easy to handle (Feeco International Organization, 2018). Limestone has poor binding properties when pelleted alone, however if an appropriate binder is used along with the limestone, relatively durable pellets can be formed. These pellets can be formed using many different techniques, where those that are formed using an agglomerator are called "agglomerates".

2.5 Size enlargement and agglomeration

Agglomeration is a form of size enlargement, a process whereby larger semi-permanent agglomerates are formed through the coalescence of smaller particles. Commonly, a binder solution is used to add to the strength of the resulting agglomerates. The binder solution is often added as a spray, where each droplet forms a small nucleus of particles. Subsequent growth is then promoted through tumbling, agitation, or compression. An alternative method of size enlargement is spray drying,

where no further agitation takes place after the particles come into contact with the binder solution. Increased compressive force applied to a mixture of the main component of the product (limestone) and the binder also results in size enlargement in the form of extrusions, such as pellets, briquettes, or tablets (Jacob et al., 2019).

Agglomerates that are formed through pressure extrusion are generally produced as long cylinders and cut to the desired length of the product. The result is a strong, highly dense, tube-shaped pellet, briquette, or tablet that will not break down easily. A major disadvantage to products of pressure extrusion, is that when the long cylinder is cut into smaller parts, a jagged edge often remains. This degrades through attrition, resulting in large amounts of dust as a waste product. This dust can also be problematic for the consumer during handling. Round agglomerates are formed through non-pressure agglomeration, such as tumble agglomeration. The product is less compact, which makes it suitable for products that are required to soak up moisture as there are more void spaces within the agglomerate, compared to that of an extrusion. A relatively spherical product can be produced through tumbling agglomeration, where the product has very few jagged edges that can break off, reducing product waste (Carlson and Kozicki, 2019). Tumbling agglomeration is therefore the most suitable for the agglomeration of micro-fine limestone, which is in the scope of this thesis.

Tumbling agglomeration is a growth agglomeration method that makes use of gravity and centrifugal forces to generate a tumbling action, setting the particles into motion to form agglomerates. Tumbling agglomerators include disc- and drum-agglomerators often used to produce granules of 1 to 20 mm in diameter. Disc and drum agglomerators generally operate in a continuous feed mode, although disc agglomerators can be more successfully implemented in continuous processes, whereas drums are better suited for batch production (Pandey, Lobo, and Kumar, 2012).

Drum agglomerators consist of a cylindrical tube that is generally set to an incline angle (β) of 10° to assist in the movement of granules through the drum. The critical speed (N_c) is the speed at which a particle in the system is held against the rim or wall of the agglomerator due to centripetal forces present in the system (Jacob et al., 2019). The drums generally run at 30-50% of the critical speed, which is dependent on the angle of inclination(β) and the diameter (D) of the drum (Equation 2.4). Drum agglomerators do not have a means to significantly control the size of the products. Manufacturing plants will therefore often have a large amount of recycling of undersized, and crushed, oversized products, which may make drum agglomerators unsuitable for commercial scale production (Green and Perry, 2008).

Disc agglomerators generally consist of a rotating and tilted disc with a rim that measures approximately 20% of the disc diameter. In order to obtain best results, the disc should be at an incline (β) of between 40° and 70° with the vertical. It is recommended to run a disc agglomerator at 50-75% N_c, as calculated using Equation 2.4 (Jacob et al., 2019; Hapgood and Rhodes, 2007; Capes, 1980; Darcovich, 2008). The critical speed is also dependant on the gravitational acceleration (g), which is equal to 9.81 m/s^2. According to Capes (1980) and Hapgood and Rhodes (2007), feed powder is introduced to the disc from the top of the inclined bed, whereas Jacob et al. (2019) and Pietsch (2002) state that it is preferable to introduce the powdered solids near the bottom edge of the rotating disc. It seems that Jacob et al. (2019) and Pietsch (2002) employ a more advantageous method, as the powdered particles will be introduced at the point where the smallest agglomerates collect during tumbling, aiding in further size enlargement.

$$N_c = 60 \cdot \sqrt{\frac{g\ sin\beta}{2\pi^2 D}} \tag{2.4}$$

Binder solution or water is added to the powdered material in droplet-form, sprayed onto the face of the disc (Jacob et al., 2019; Hapgood and Rhodes, 2007). Scrapers are used at an angle to rotation in order to maintain a uniform protective layer of product over the surface of the disc and control the flow pattern of material. Using scrapers also ensures that the powdered material does not remain pressed against the rim of the disc as a result of centrifugal forces in the system (Capes, 1980). Disc agglomerators have a unique feature compared to drum agglomerators, in that they allow for a size classification effect. The smaller particles sift to the bottom of the disc and through increased friction, the larger agglomerates are carried towards the top of the disc. With a continuous operation, those that are of an appropriate size (decided by the set-up of the agglomerator), are discharged over the rim of the disc and the smaller agglomerates are retained for continued growth (Pietsch, 2002). Drum agglomerators do not have this property, leading to a wider size distribution of the products.

Tumbling agglomeration processes often make use of wet agglomeration, where liquid bridges of binder solution are exploited to form agglomerates through centrifugal forces and tumbling. Wet agglomeration can be divided into three sub-processes that happen simultaneously throughout the entire process, namely: (1) wetting and nucleation, (2) consolidation and growth, and (3) breakage and attrition (Jacob et al., 2019; Hapgood and Rhodes, 2007).

Wetting refers to the first process in agglomeration, where the liquid added to the system replaces

some of the air voids between the dry particles. Nucleation then occurs when liquid bridges form between the particles to form small nuclei of the agglomerates. When a sufficient amount of liquid is added to a system of dry particles, inter-particle liquid bridges form, assisting in agglomeration. Four types of liquid states, namely pendular, funicular, capillary and droplet, can be present in the system depending on the proportion of liquid present between the particles. In the pendular state, there is only enough liquid in the system to form a point contact and concave menisci between the particles. This allows the surface tension of the liquid to draw the particles closer together, resulting in strong boundary forces. As the proportion of liquid to dry particles increases and the system enters the furnicular state, the attractive forces between the particles are decreased as a result of the increased free movement of the liquid. As the system becomes saturated with liquid (capillary and droplet states), the strength of the nucleus structure is very low due to the lack of curved liquid surfaces and fewer boundaries for surface tension to act on. Agglomerates formed by liquid bridges are however not usually the end product, but resulting solid bridges formed in and between nuclei in the pendular state can give rise to strong agglomerates (Hapgood and Rhodes, 2007; Simons, 2007).

The liquid bridges and concave menisci that form between the solid particles when moisture is added to the system often form solid bridges through drying, reacting or changing phase with changes in temperature. The liquid added may also contain a binder, adding strength to the liquid and stronger solid bridges that form. Collisions between these nuclei, the nuclei and the feed powder, or the nuclei and the equipment cause an increase in granule density, due to closer packing of the particles. These collisions can also allow the nuclei to attach to one another, or additional powdered particles, causing the agglomerates to increase in size. This is the second process in agglomeration, consolidation and growth.

Breakage of the agglomerates can be caused by breakage of the wet agglomerates in the agglomerator, or it can be caused by attrition of the dried agglomerates in the agglomerator or due to subsequent handling. In wet agglomerates, breakage occurs due to collisions between the agglomerates or between the agglomerates and the equipment. It influences and may control the size distribution of the agglomerates that are produced. Attrition of the dry agglomerates can be caused by insufficient bonding of the particles during the agglomeration process and is generally undesirable. The final product formed during agglomeration is however a combination of these three sub-processes that take place simultaneously throughout the main process (Iveson et al., 2001; Hapgood and Rhodes, 2007; Jacob et al., 2019).

Agglomerates produced on a commercial scale are commonly produced in a closed loop system, where the product is formed in a disc agglomerator and undersized fines are recycled back into the system to minimise wastage. Figure 2.2 is a simplified flow diagram showing the closed-loop nature of this process. The closed loop process starts at the point where the undersized product is recovered and recycled back to the feed. The raw material and the recycled product are homogenised in a pin mixer where, if a dry binder is used, the binder is added to the mixture. This mixture is added to the inclined disc agglomerator where moisture is added to the system and the agglomerates are produced. The image shows the agglomerator in rotation, where the smaller agglomerates are in continuous rotation and the larger agglomerates are to be expelled from the agglomerator. In a continuous process, those that are expelled from the agglomerator are collected and dried, whereafter they are screened and the closed loop process is continued or the agglomerates are stored for use (Albert and Langford, 1998).

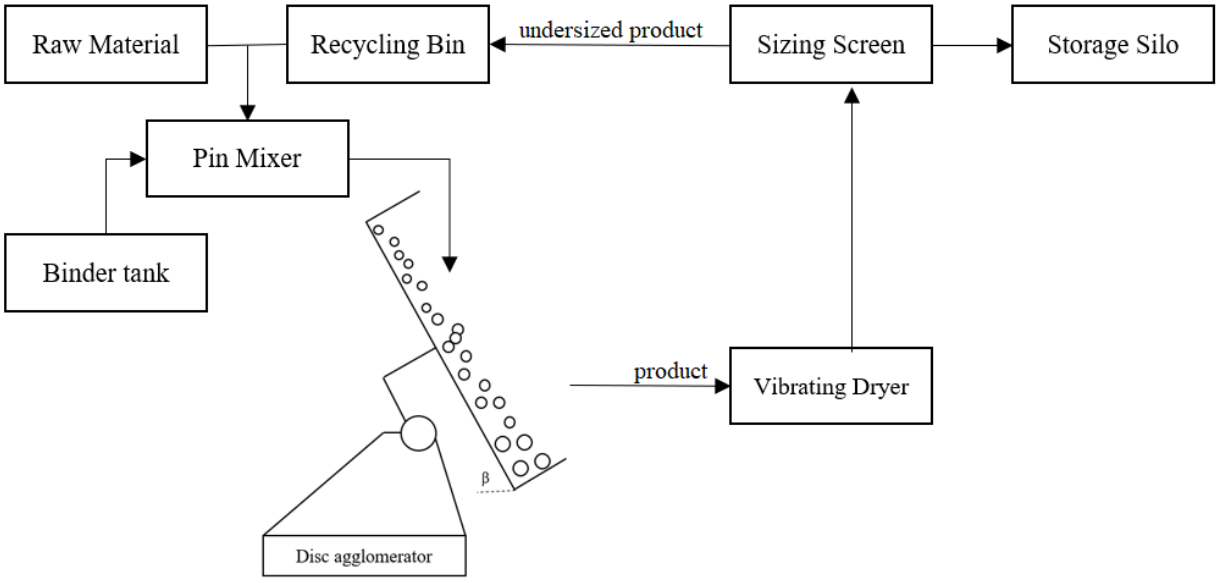


Figure 2.2: A standard closed loop system for the agglomeration of limestone pellets (Adapted from Albert and Langford (1998)).

2.6 Binders and types of binders investigated for limestone agglomeration

During transportation and handling, agglomerates are often exposed to forces that may cause them to abrade or break. Examples of when limestone agglomerates that are applied to the soil are exposed to significant amounts of forces would be when they are poured into storage units, packaged, packed into and unpacked from transportation vessels, and applied to the soil using agricultural spreading equipment. When the agglomerates do not sufficiently resist abrasion and breaking, they disintegrate into dust fines. These dust fines can be problematic as they are no longer what the consumer expected, and may cause inaccuracies in limestone dosing to the soil. Dust fines from the agglomerates can therefore be regarded as product waste. In order to mitigate product wastage, binders are used. Binders are defined as substances that adhere chemically or physically to the solid surfaces of a product, forming a material bridge between its particles (Pietsch, 2002).

During agglomeration, natural adhesion forces between particles are significantly increased when moisture is added to the system and liquid bridges are formed (Simons, 2007; Pietsch, 2002). Stronger solid bridges are formed when a large proportion of the liquid is removed from the system, resulting in an even stronger product. These bridges can be made stronger through the use of a liquid binder, or a binder that is added as a dry powder and actioned through the addition of a liquid. The viscosity of the liquid or liquid binder has a great influence on the agglomeration process. A binder with a higher viscosity will have more gel-like properties, but a higher viscosity will also form a less compacted pellet due to the decreased mobility of the fluid. This decreased fluid mobility results in a broad distribution of pellet sizes and shapes (Belwal et al., 2016), whereas the size and shape of the agglomerates that are used as a commercial product should be relatively uniform.

Agglomerates that are used as soil amendment products in agriculture should make use of binders that are non-toxic to the environment and crops. In order to treat soil acidity with the use of limestone, the binder should also not cause acidification, counteracting the action of the limestone. It should also not negatively impact the soil properties when applied to the soil repeatedly over long periods of time. The resulting agglomerates should be strong enough to resist impact, compression, and abrasive stresses associated with the process prior to application, such as during packaging, transportation and application. They should however also be able to disintegrate under the influence of natural weathering and soil moisture, post-application (Jovanovic et al., 2016). Binder selection is however

also dependent on economic factors, where by-products or wastes of different processes could result in the use of cheap binder alternatives. The binder selection should also take into consideration the availability of the product in the region that the agglomerates will be produced. Although effective, binders are therefore often non-viable for use when transportation and product costs result in an unaffordable product.

2.6.1 Sodium alginate

Sodium alginate is a non-toxic, biodegradable, organic binder (Pietsch, 2002) extracted from *Ecklonia maxima*, a fast growing brown seaweed species that grows off the coastline of southern Africa. The availability of brown seaweed off the coast of South Africa, makes it easily accessible for the manufacture of alginates. Once harvested, the alginate can be recovered from the biomass relatively easily (Lesser, 1950).

Alginate is an anionic polymer that consists of α-L-guluronic and β-D-mannuronic acids. It can be used in the agglomeration of limestone, because the alginate polymers form gels when they come into contact with multivalent ions, such as Ca^{2+} found in limestone ($CaCO_3$). Alginate gels are formed when the monovalent sodium ions from the guluronic acids are exchanged with these divalent, calcium ions from the limestone. Figure 2.3 shows the sodium alginate polymers before they come into contact with the Ca^{2+} ions and how ionic cross-linking happens and the Ca^{2+} ions replace the Na^{+} ions on the guluronic acids. The two polymer strands then fit together into a block-like structure, similar to an egg in an egg carton. These polymer strands can bond to multiple Ca^{2+} ions on its surfaces to form a 3-dimensional gel network, in this case ultimately bonding the limestone particles to form an agglomerate. This process does not require any heat or external stimulation, making it relatively easy to use in the production of limestone agglomerates (Russo, Malinconico, and Santagata, 2007; Rinaudo, 2008; Paques et al., 2014).

The stiff property of the calcium-alginate product can be exploited in the production of agglomerates, as it has been used as a binder for various dry components in the production of tablets in the pharmaceutical industry, as well as for animal feed. According to the scientific opinion of Rychen et al. (2017b), sodium alginate can be safely used as a binder in dog pellets with a recommended maximum concentration of 40 g/kg pellets. Sodium alginate was investigated as a binder by Rodriguez-miranda (2012), where it was found a 2% sodium alginate solution used as a binder, produced a fish feed product with strength properties appropriate for commercial use. However, sodium alginate has not been

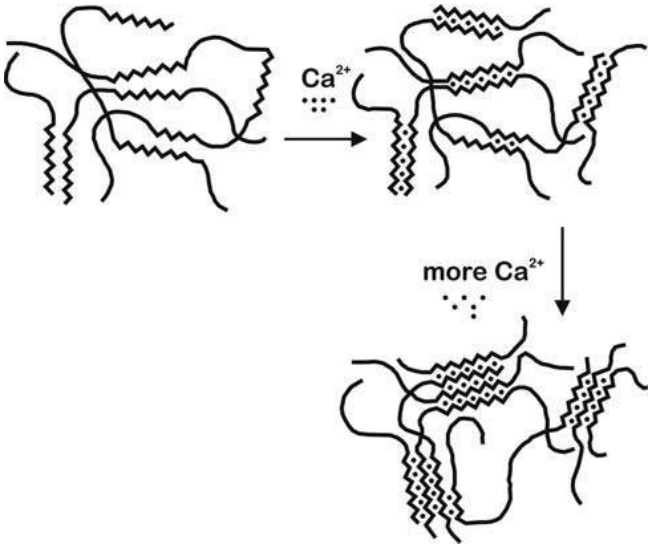


Figure 2.3: The egg-carton model for the gelation of sodium alginate polymer strands when they come into contact with bivalent calcium ions. (Reprinted with permission from Paques et al. (2014). Copyright 2014 Elsevier B.V.)

deeply investigated as a binder for soil amendment products. But, being a non-toxic, biodegradable, and organic compound, it does not pose a risk for the environment and therefore has potential as a binder for limestone agglomerates to treat soil acidity (Rychen et al., 2017b).

2.6.2 Lignosulphonate

Lignin is an alkyl-aromatic bio-polymer that strengthens and waterproofs the secondary cell walls in terrestrial plants. It is one of the most readily available bio-polymers on earth and its removal is a key step in the production of paper and the conversion of biomass to biofuels (Kang et al., 2019). With more than 70 million tons produced by the pulp and paper industry annually, less than two percent is recovered for use as a chemical product (Lora, 2008; Guterman, Molinari, and Josef, 2019). Lignin has a high carbon content and numerous functional groups (hydroxyl, carbonyl, carboxyl, methoxyl) (El Mansouri and Salvadó, 2007; Qi et al., 2019) with various amounts and proportions, leading to different compositions and structures of lignin. Although it is readily available, it is extracted from plant matter with ill-defined molecular structures. The properties of the product are therefore heavily reliant on the source and extraction method used to obtain the lignin (Guterman, Molinari, and Josef, 2019).

Lignosulphonates are the most abundant type of industrially used lignin product. It is a cellulose-based organic component of trees that is the dominant by-product of the sulphite-based, paper pulping process (Veverka and Hinkle, 2001). A solution of sulphites or bisulphites digest wood, where 4-8% sulphur is incorporated into the lignin molecules, mostly in the form of sulphonate groups (Lora, 2008). In contrast to its origin, lignin, the lignosulphonate produced in this way is water soluble (Ekeberg et al., 2006). Figure 2.4 shows the chemical structure of a lignosulphonate molecule.

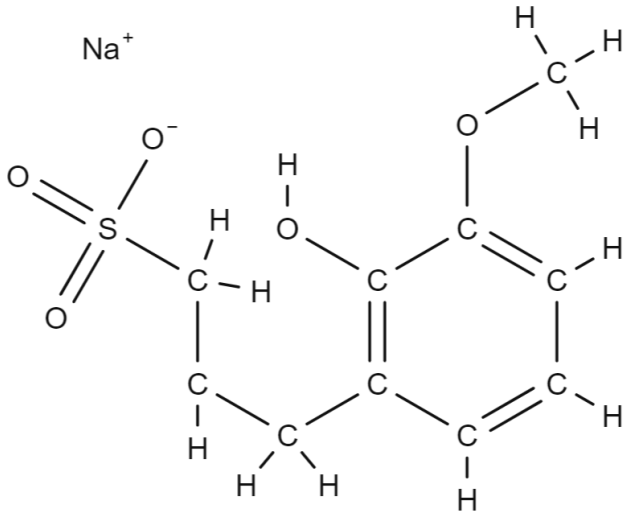


Figure 2.4: The chemical structure of lignosulphonate, showing the water-soluble sulpho-groups (PubChem CID: 25113562)

According to Nedosvitii et al. (1994) and Madad et al. (2011), the specific properties that are associated with lignosulphonates can be related to the presence of some of the functional groups in them. The sulpho-groups that are added during pulping can be seen in Figure 2.4 and are mainly responsible for the water soluble nature of lignosulphonate (Lora, 2008; Madad et al., 2011). Industrially produced lignosulphonate is in powder-form, however, being water-soluble, it can be made into a solution for use as a binder in the formation of agglomerates. The lignosulphonate solution relies on adsorption as a bonding mechanism and readily attaches to the surface of the adsorbent, in this case limestone, reducing its surface tension. As a result of the adsorption, the adsorbed lignosulphonate solution on the surface of the limestone powder is thickened and hardened, strengthening the forming agglomerates (Nedosvitii et al., 1994). Lignotech Borregaard, a leading lignosulphonate producer, states that lignosulphonate does not require any heat or external stimulation to act as a binder, making it suitable for non-pressure agglomeration, such as in an inclined disc agglomerator.

Sappi, the well-known paper suppliers, are major lignin and lignosulphonate suppliers from their Tugela Mill in South Africa. It is therefore a readily available product in South Africa and is known to be one of the most commonly used binders in the animal feed industry, but has also been used in the agglomeration of limestone (Albert and Langford, 1998). It is also commonly used as an additive to concrete to reduce the amount of water required for mixing and handling (Ekeberg et al., 2006; Lora, 2008). Although lignosulphonate has been used as limestone binder, it has not been deeply investigated. The European Food Safety Authority (2015) assessed the impact that lignosulphonate had on the strength of animal feed pellets. It was concluded that 7.5 g of lignosulphonate per kilogram of animal feed resulted in pellets that were durable enough for commercial use. ICF International (2013) assessed the impact that lignosulphonate had on the environment, with regards to soils and concluded that soil micro-organisms, enzymatic reactions, and ultraviolet radiation contribute to the decomposition of lignosulphonates in a similar way to rotting wood, posing negligible threat to the environment. Along with the negligible effect that lignosulphonate has on the environment, its water-soluble nature can be exploited for a binder used in the manufacture of soil amendment products, such as limestone agglomerates. The binder can solubilise in rain or irrigation water, leaving the agglomerate to disintegrate, and the limestone accessible to the soil as fine particles with a larger surface area to neutralise soil acidity.

2.6.3 Bentonite

Smectite is the name given to a group of sodium-, calcium-, magnesium-, iron- and lithium aluminium-silicates. Clay minerals, including montmorillonite, saponite, and nontronite are included in this group. Bentonite is defined as a naturally occurring material that is dominantly comprised of the clay material, smectite - usually in the form of the mineral, montmorillonite ($Al_2Mg_3Si_4O_{10}(OH)_2 \cdot nH_{20}$) and it depends on this mineral for majority of its physical properties.

Figure 2.5 shows the structure of montmorillonite, as this is the main component of bentonite. It is however also made up of quartz, feldspar, organic matter, gypsum and pyrite (Liu, Xie, and Qin, 2017; Tabil, Sokhansanj, and Tyler, 1997; Clem and Doehler, 1961). A single montmorillonite is made up of a lattice consisting of two silica tetrahedral sheets. The sheets allow adsorption of available water, prying the adjacent sheets apart, resulting in an increase in overall volume of the clay. This swelling action provides the basis for many valuable uses of clay in industry, where many different industries exploit the fact that the properties of a bentonite-water mixture changes as the ratio of bentonite to water changes. Bentonite that is mixed with relatively small amounts of water forms a mixture

with strong adhesive properties, but the more water that is added to the mixture, the more plastic the mixture will become. It is for this reason that bentonite can be added as a constituent to other materials, such as limestone and water, to form strong agglomerates through the pendular state of agglomeration and is commonly used as a binder in the metallurgical and animal feed industries (Clem and Doehler, 1961).

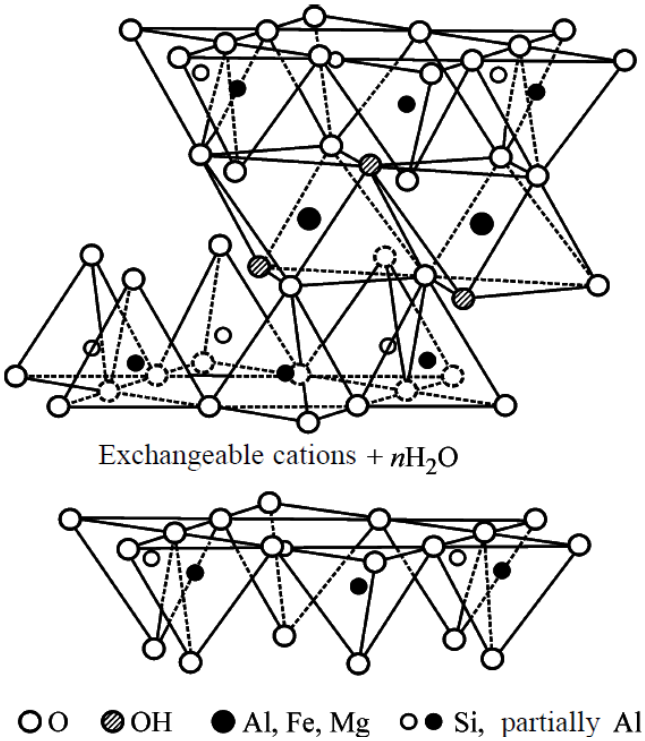


Figure 2.5: The structure of montmorillonite, the main constituent of bentonite (Reprinted with permission from Golubeva, Korytkova, and Gusarov (2005), Copyright 2005, Springer Nature).

According to Liu, Xie, and Qin (2017), pellets that are dried and roasted with bentonite are known to have the strength properties to meet transportation requirements and can absorb water up to 15 times its dry mass. As the bentonite absorbs water and swells, the clay particles decrease in size, resulting in an increase in the number of particles per unit mass, further resulting in an increase in available surface area of the clay particles. The larger surface area of the clay particles allows for increased area for adsorption of nutritious liquids or insecticides that can be applied to the soil (Clem and Doehler, 1961).

Bentonite was assessed as a binder for animal feed, by Rychen et al. (2017a), where a bentonite concentration of 1-5% was recommended to produce animal feed of acceptable pellet durability. The impact that bentonite had on the environment was also investigated and it was concluded that because bentonite is a natural component of the soil, its use as a binder would not adversely affect the environment. It can therefore be considered in the production of soil amendment products (Jovanovic et al., 2016).

2.7 Lime requirement

McLean (1973) defined the limestone requirement for soil as, "the amount of lime or other base needed to neutralise the undissociated and dissociated acidity in range from the initial acidic condition to a selected neutral or less acidic condition." Therefore, the lime requirement is the calculated amount of limestone that should be applied to the soil to relieve soil acidity to a selected condition that would be acceptable for crop growth.

The selected condition is dependent on the crop supported by the soil, as well as exchangeable aluminium - to prevent aluminium toxicity (Reeve and Sumner, 1970). The lime requirement has also been known to alter with economic considerations, where the amount of liming material required is selected to maximise economic return (Hesse, 1971). Determining the lime requirement for an acidic crop land can be difficult when there are many of these factors to consider. Accuracy can also be a problem, where different methods have been developed for different regions. Using a method that is not suitable for the soil that is being tested, may result in an over-, or under-estimation of limestone required to treat its soil acidity. Various different methods have been used throughout the world and throughout history, where the South African agricultural industry is often unsure which lime requirement method should be used in the different climates present in the country (van der Berg, Hardie, and Raath, 2017).

The Shoemaker-McLean-Pratt (SMP) buffer method is the most commonly used method in the United States of America to determine the lime requirement. This buffer method was originally developed as a means to do routine soil testing in a laboratory, proving to take less time than other methods used at the time. The resulting pH of the buffer was used as a determining factor in the lime requirement, rather than the soil itself (Shoemaker, McLean, and Pratt, 1961). As with many other lime requirement buffers, the buffer used in this test contains potassium chromate and paranitrophenol, both toxic compounds, making the procedure relatively undesirable to carry out (Hoskins and Erich, 2008; Wolf,

Beegle, and Hoskins, 2008).

As soils differ throughout the world, lime requirements should be adapted for the region in which it is being used. Eksteen (1969) developed a lime requirement method specifically for South African topsoils (the top 15 cm of the topsoil) in the winter rainfall region of the Western Cape. Soils in this region are known to have low levels of organic matter (Smuts, Lambrechts, and Saayan, 2001). This method is based on the ratio between the extractable calcium and magnesium in the soil, and the extractable acidity. The ratio is called the R-value, where an optimum R-value is suggested for different crop types. This follows the principle that every crop has a different balance of basic cations and soil acidity for optimum growth and yields (Smuts, Lambrechts, and Saayan, 2001). The Eksteen method is capable of determining the lime requirement for soils where the pH is to be higher than pH 5. The exchangeable calcium and magnesium are extracted with a buffered ammonium acetate (NH_4OAc) solution and the soil acidity is determined through a titration of a K_2SO_4 solution that is leached through the soil, and NaOH. The values obtained through these tests are compared to the required R-value for the specific crop grown, where the additional base cations needed to obtain the R-value is used to determine the lime requirement (Eksteen, 1969; Smuts, Lambrechts, and Saayan, 2001). Eksteen (1969) states that an R-value of 1.5 is acceptable for soil that supports potatoes, whereas wheat would require an R-value of 3. Vegetables, fruits and lucerne would make use of 5, 10 and 15 as appropriate R-values, respectively. It is however common practice to make use of an R-value of 10 when conducting laboratory-scale experiments.

2.8 Movement of limestone through soil

Understanding the movement of limestone through a soil profile is important to understand how the limestone will impact the soil deeper than at just the surface. This is to identify whether or not, with the application of surface applied lime, amelioration of soil acidity can take place below the topsoil (deeper than 25 cm) and at the root zone (this differs between crops, but is $\approx$ 100 cm deep for wheat) to reduce the risk of aluminium toxicity.

In 1992, an 18 year field experiment began where Li et al. (2019) initiated a study investigating the long-term effect of surface application of limestone on sub-surface soil acidity. The researchers hypothesised that keeping the top 10 cm of soil at pH 5.5, through long-term surface application of limestone, would lead to the improvement of sub-surface soil acidity over time. The liming made use of fine ($\leq$ 250 μm) agricultural limestone that was applied every 6 years to maintain a pH 5.5 in

the top 10 cm. Lime requirement tests were carried out where it was calculated that 0.71 t/ha would ensure that the correct amount of limestone was added to the soil.

In the 12 months after the initial liming, the topsoil pH increased sharply as determined by the lime requirement. Over the six years after liming, the pH in the topsoil slowly decreased. Although there was no significant difference found between the pH at 10-15 cm and 15-20 cm, the pH of these zones did increase in the order of 0.03 pH per year after liming. Only after 12 years did the differences in pH between the unlimed control and the limed plots show, but these differences were confined to the top 20 cm of the soil profile. Only in the 18^{th} year were significant differences found between the control and the limed plots at depths between 20-30 cm.

This supports previous experimental research, where Moschler et al. (1973) applied limestone to the surface of a grain crop land. Although the grain yield increased by roughly 30% after the limestone was applied, no significant changes of soil pH were observed when soil samples were collected to a depth of 20 cm in 10 cm increments. This suggests that the limestone remained on the topsoil and did not filter through the soil profile. Blevins, Murdock, and Thomas (1978) experienced a similar outcome, but a change in pH at a depth of 30 cm was observed when limestone was applied at 3 times the lime requirement. This suggested that the movement of limestone through a soil profile was dependent on the rate at which it was applied, although, this may not be economically viable for farmers on a commercial scale.

The work done by Li et al. (2019) indicates that time plays a significant role in the movement of limestone through a soil profile. This is supported by Edwards and Beegle (1988) in which a change in pH in only the top 5 cm of the soil for the first 4 years after liming was observed. Only after the 4 year period post-application of limestone, was there an increase in the soil pH in the 5-10 cm region of the soil profile. The frequency of limestone application in the experimental research carried out by Edwards and Beegle (1988), did not have an effect on the movement of limestone, but did have an effect on pH in the topsoil.

The implication of the results obtained in these research experiments pose the question of whether or not an even finer limestone will relieve soil acidity at levels deeper than the top 5 cm more quickly? Limestone can ameliorate soil acidity in two ways: 1) soil acidity is neutralised when it comes into contact with the limestone, or 2) the limestone can slightly dissolve in the water, making the soil water more alkaline. This alkaline water can then neutralise soil acidity at levels deeper than the soil surface as it moves through the soil profile. Micro-fine limestone may be more likely to move between the

soil particles along with the water filtering down the soil profile, than that of a less fine limestone. This may give it the opportunity to treat soil acidity through the solid-liquid interface at levels deeper than the top 5 cm of the soil. With that, although limestone has low solubility, a micro-fine limestone product may dissolve in the soil water more easily than that of a less fine limestone investigated in literature. This introduces the possibility of using micro-fine limestone to treat soil acidity at not only the top soil, but lower down in the soil profile as well, hence further research pertaining to the use of micro-fine limestone was undertaken in this thesis.

2.9 Literature summary

Along with other factors, soil acidification is a consequence of ammonium-rich fertilisers, acid rain and the decomposition of plant matter. With an increase in H^+ ions added to the soil, the pH of the soil can drop to levels low enough to increase the solubility of heavy metals. Aluminium toxicity is a major risk to crop health, especially when in the root zone. It is therefore necessary for farmers to ensure that soil pH remains at manageable levels, where soil acidity can be treated through liming. The carbonates added to the soil through added limestone react with the available H^+ ions, relieving soil acidity through the release of H_2O and CO_2.

Limestone is often applied as a powdered product, where product losses often occur when it is applied in unfavourable or slightly windy conditions. In order to be sure that the correct amount of limestone that was calculated to be applied to the soil, was in fact applied to the soil, these losses should be mitigated. Using agglomerated limestone is a means of applying limestone to the soil, where the added weight in it being an agglomerate and the bonds between the finer particles prevent these losses. When the limestone is of the correct size (2-6 mm), it can be easily applied to the soil surface using conventional agricultural spreading equipment. Agglomeration methods, such as with the use of an inclined disc agglomerator, can be used in the production of these limestone agglomerates.

The limestone agglomerates should remain intact from production to application, made possible with the addition of binders. The binders should add strength to the limestone agglomerates so that they can resist breaking under impact, abrasive, or compressive forces that they may experience during the packaging, transportation and storage processes prior to application. Ionic cross-linking between sodium alginate polymers and divalent calcium ions has the potential to form strong bonds between the limestone particles, making sodium alginate an attractive binder for limestone. Lignosulphonate, a by-product of the paper pulping industry, is a water soluble product that can easily be applied

as a binder solution in the agglomeration process. It is easily adsorbed onto the surfaces of the other constituents in a system, such as limestone particles, allowing it to bond the particles in the formation of agglomerates. Lignosulphonate has been used as a binder for limestone agglomerates in industry, making it an attractive binder for further investigation. Bentonite is a cost effective binder option, known for its swelling capabilities when in contact with water, allowing for the adsorption of limestone during the agglomeration process. It is commonly used as a binder in various industries, namely in the production of animal feed and metallurgical pellets, making it a potential alternative for use in the agglomeration of soil amendment products.

Literature shows that when fine limestone is applied to the surface of the soil, little movement through the soil profile occurs. Studies show that after liming, there were only significant changes in pH in the top 10 cm of the soil over long periods of time. It is however ideal to have soil acidity ameliorated throughout the soil profile, from the soil surface to the root zone. Micro-fine limestone should therefore be investigated to determine if the finer limestone particles can move through the soil profile more readily than that of more coarse limestone used in previous studies.

This thesis therefore investigated the use of agglomerated micro-fine limestone to combat the difficulties associated with transportation, handling and application of conventional limestone. The mitigation of these handling difficulties should be investigated through with the addition of binders. However, the advantage of having an increased surface area with the use of micro-fine limestone should also be considered. The agglomerates should therefore also be able to disintegrate when exposed to environmental conditions, leaving the micro-fine limestone to neutralise soil acidity and possibly move through the soil profile. The surface application of these agglomerates should therefore be investigated to determine if micro-fine limestone ($\approx$32 μm) particles, or alkaline water as a result of dissolved micro-fine limestone, can ameliorate soil acidity at levels deeper than the surface.

Chapter 3

Research objectives and thesis overview

Aim

The aim of this project is to develop an inclined disc agglomerator and produce micro-fine limestone agglomerates used to ameliorate soil acidity. They should be produced with a maximised yield in a suitable size range that allows them to be spread with conventional agricultural spreading equipment. Sodium alginate, lignosulphonate and bentonite should be included in the production of the agglomerates to assess how the binder types and concentrations thereof impact the overall strength of the agglomerates. The surface application of the stronger agglomerate types for each binder type should be assessed in the amelioration of soil acidity at different depths of a soil profile. This is to determine if agglomerated micro-fine limestone can be used to mitigate product losses during the application of powdered limestone, while also ameliorating soil acidity at depths deeper than the soil surface.

Research objectives

The main aim of this research is to develop agglomerates of micro-fine limestone used to neutralise acidic soil. In order to achieve the overarching aim, the following objectives were identified which, if achieved, will further the aim of the project.

- Design and manufacture an inclined disc agglomerator. Determine the impact that the operating parameters of the inclined disc agglomerator and the agglomeration process have on the manufacture of micro-fine limestone agglomerates with a maximised yield of product with a diameter in the range of +2 -6 mm.
  This will allow for the production of agglomerates with a maximised mass fraction similar in size to those that should be used on a commercial scale as they can be applied to the surface of

the soil using commercial agricultural spreading equipment.

- Determine how the binder type and concentration thereof impacts the strength properties of the agglomerates and determine which of the agglomerate types will be able to resist breaking when exposed to stresses involved in the processes prior to application.
  Determining how the binder types and concentrations thereof contribute to the strength of the agglomerate products will also determine which of the agglomerate types will be strong enough to withstand the impact, abrasive and compressive forces that they may experience during production, packaging, and transportation. The disintegration of the agglomerates when exposed to moisture will also assist in determining if the agglomerates will disintegrate prior to or after application when wet.

- Determine if and how the agglomerates of suitable strength disintegrate under the application of simulated rainfall in order to increase the pH of the soil at levels between the surface topsoil (< 25 cm).
  This will determine if the agglomerates of micro-fine limestone are suitable for application to the surface of the soil and if they disintegrate sufficiently to exploit the large surface area of the micro-fine limestone to ameliorate soil acidity at levels deeper than the surface.

Scope

The scope of this project included the design and manufacture of an inclined disc agglomerator for the production of limestone agglomerates. Sodium alginate, lignosulphonate and bentonite were included at different concentrations, as binders for added agglomerate strength. Strength testing equipment and software were designed and commissioned, to assess the impact, abrasive, compressive and moisture disintegration strength of the produced limestone-binder agglomerates. Lab analysis was undertaken for many different aspects of this thesis, one being to obtain data from soil collected from Caledon (South Africa) as a determining factor in artificial soil column experiments. These soil columns were designed and manufactured, alongside an automated rain simulator, to assess the movement of micro-fine limestone through packed soil when exposed to three months of simulated rainfall.

Thesis overview

- Chapter 1 covered the introduction to this thesis. It gives a brief overview of the motivation for the research and a discussion of how the research was carried out.
- Chapter 2 covered the literature review and industrial knowledge on the topic at hand. The soil and acidification thereof was discussed, as well as how soil acidification is handled in industry. Different types of limestone and binders that can be used in the agglomeration of limestone were discussed. Size enlargement and the process of agglomeration was discussed in this chapter, especially pertaining to the agglomeration of limestone. Research that has been done on the surface application of limestone was discussed, leading to the research question of whether or not micro-fine limestone could be used in agglomerate-form to mitigate product losses experienced during the application of powdered limestone, while also serving its purpose of ameliorating soil acidity.
- Chapter 3 contains the aim, research objectives, and scope of this research project.
- Chapter 4 gives an overview of the materials and methods that were used to carry out repeatable experiments. This chapter includes the experimental set-up used to optimise the agglomeration process of the lime agglomerates. The methods used to assess the strength of the produced agglomerates were presented, where further investigations into how the strong agglomerates were used to test the effect that they had on a soil profile are described.
- Chapter 5 includes discussions of the results obtained from the research. The objective of this chapter was to obtain parameters to maximise the mass fraction of agglomerates of a suitable size produced during agglomeration. Also, to determine which of the agglomerates were strong enough to be considered for commercial use. This section also included discussions on how the limestone agglomerates impact the pH of a soil profile.
- Chapter 6 is included at the end of the document body, where the conclusions of the research were presented and recommendations for future work were made.

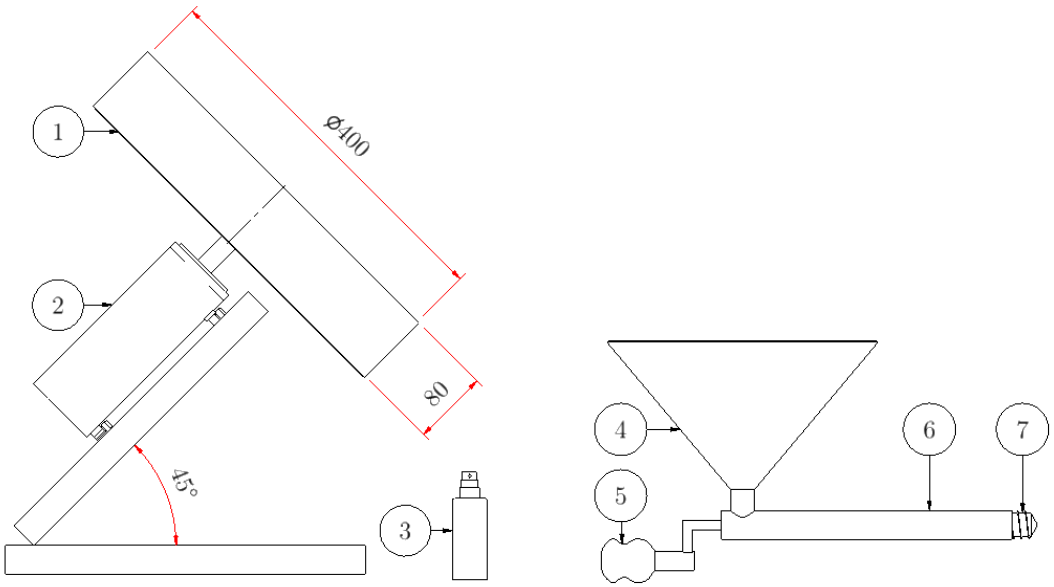
Chapter 4

Materials and Methodology

4.1 Introduction

This chapter describes the methods that were followed in order to obtain the results required to satisfy the objectives of the project. An inclined disc agglomerator was designed and manufactured, whereafter parameters were obtained to maximise the mass fraction of agglomerates produced within the +2 -5.6 mm diameter range. The parameters that were assessed were, (1) speed of rotation of the inclined disc, (2) volume of liquid, and (3) the concentration of binder added to the system. Micro-fine limestone and binder (sodium alginate, lignosulphonate, and bentonite) agglomerates were then manufactured at different binder concentrations in the disc agglomerator using these parameters. Those agglomerates that were produced in the desired size range underwent strength testing. Four tests were carried out to determine which of the binder types and concentrations thereof produced agglomerates that were strong enough for industrial use. The agglomerate types that performed the best for each binder type where applied to artificial soil columns, in masses that were determined using a lime requirement test. The agglomerates that were placed on the artificial soil columns underwent a 14-week rain simulation to determine if and how the limestone ameliorated soil acidity once the agglomerates had disintegrated.

The agglomerates were produced in an inclined disc agglomerator, designed and manufactured as per design specifications set out by Capes (1980). A manually-driven screw conveyor was used alongside the agglomerator for application of dry powder to the system. A schematic of the agglomerator and the screw conveyor are shown in Figures 4.1a and 4.1b.



(a) Schematic of the disc agglomerator.

(b) Schematic of the screw conveyor.

Figure 4.1: The components of equipment used in the inclined disc agglomeration system. The disc (1) was set to an angle of 45°, driven at 37.5 rpm by a SEW R17 DT63K4 geared motor (2). A spray bottle (3) is used to add liquid to the system. The powder was placed in the funnel (4), when the handle (5) on the conveyor was turned, the screw (7) rotated to move the powder along the tube (6) to the outside.

The disc (1) had a diameter of 400 mm and rim height of 80 mm. It was made from polyvinyl chloride plastic (PVC) and driven by a SEW R17 DT63K4 geared motor (2) controlled by a variable speed drive. The inclination angle of the disc was set to 45°, in accordance with many literature sources (Russo, Malinconico, and Santagata, 2007; Cuq et al., 2013; Capes, 1980; Belwal et al., 2016). A 50 mℓ spray bottle (3) was used to apply the liquid to the system during the agglomeration process. The manual screw conveyor, in Figure 4.1b, was placed near the disc so as for the powder to fall to the bottom right of the disc when it was rotated in the clockwise direction. This was to ensure that the added powder aided the growth of the smaller agglomerates, rather than to fall where the larger agglomerates collected. For each run, a portion of the powdered constituents was placed in the funnel (4). The screw (7) rotated as the operator turned the handle (5), moving the powder through the thread of the screw to the disc. This allowed smaller quantities of powder to enter the system at a time, rather than in larger batches if poured onto the disc.

All reagents used in the production of agglomerates were of minimum reagent grade and were sourced from Sigma-Aldrich, unless otherwise stated. Lignosulphonate was obtained as a by-product of the South African paper pulping industry and bentonite (94% sodium montmorillonite, 5.5% quartz, 0.5% mica) was obtained from Imerys Refractory Minerals. The sodium alginate that was used had a purity of 87.2 ± 0.2%, as per the Sigma-Aldrich catalogue. Micro-fine agricultural lime powder was obtained from Equalizer AG, and had a mean particle size of 32.40 μm and a size distribution presented in Figure 4.2, as determined with a laser diffraction particle size analyser. Table 4.1 shows the chemical composition of the dry powdered binders and limestone, as determined through major element X-Ray fluorescence (XRF) analysis. The water that was used for the production of the agglomerates and throughout all the experiments that they underwent, was reverse osmosis (RO) water with a conductivity of ≈ 3 μS/cm.

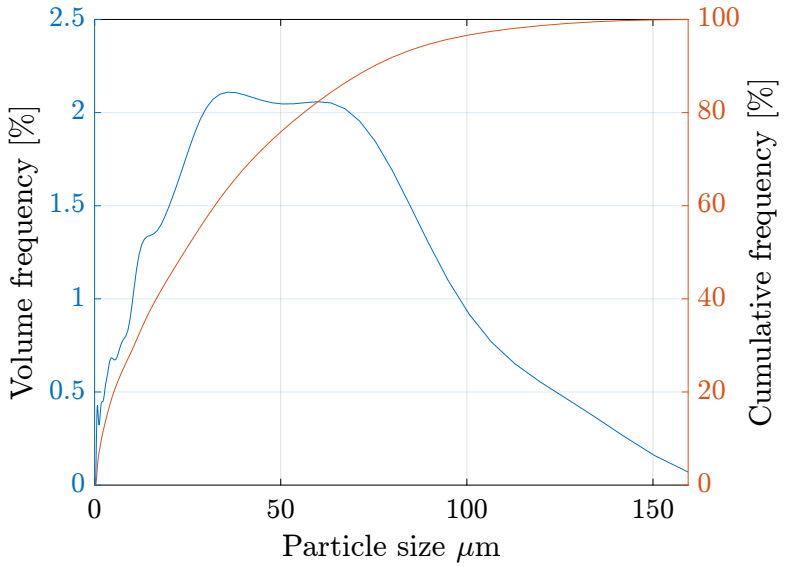


Figure 4.2: The volume frequency (blue) and the cumulative (red) particle size distribution for the agricultural lime used in this study, as determined through laser diffraction. The curves represent the average of 3 technical replicates with error bars negligibly small.

Table 4.1: The chemical composition of the agricultural lime (Ag-lime) and powdered binders - sodium alginate (Na-A), lignosulphonate (LS) and bentonite (B) - as determined by XRF for selected major element analysis.

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
Ag-lime	0.61	44.86	1.58	0.07	8.15	0.26	0.05	0.02	4.82	0.12
Na-A	1.26	0.59	0.04	0.20	0.12	-	6.52	0.01	4.09	0.05
LS	0.01	0.01	-	0.87	-	-	11.15	0.07	0.39	0.01
B	14.60	1.12	2.88	0.80	3.15	0.05	2.25	0.03	58.05	0.20

The XRF results show that calcium oxide (CaO) and magnesium oxide (MgO) make up 44.86% and 8.15% of the agricultural lime, respectively (R_{XRF}). It was assumed that CaO and MgO, with molecular masses (M_{oxide}) of 56.0774 and 40.3044 g/mol, was bound to CO_2 as $CaCO_3$ and $MgCO_3$, with molecular masses ($M_{carbonate}$) of 100.0869 and 84.3139 g/mol, respectively. Therefore with Equation 4.1 and the respective molecular masses, the agricultural lime was determined to have a $CaCO_3$ purity of $\approx$ 80%. Equation 4.2 was used to calculate the amount of Ca^{2+} and Mg^{2+}, with molecular masses ($M_{elemental}$) of 40.078 and 24.305 g/mol, to determine if the limestone was dolomitic or calcitic. It was therefore determined that the limestone powder consisted of 32.06% Ca^{2+} and 4.914% Mg^{2+}, showing that the limestone used in this study was calcitic limestone.

$$\%_{carbonate} = R_{XRF} \cdot \frac{M_{carbonate}}{M_{oxide}} \cdot 100\% \tag{4.1}$$

$$\%_{Ca/Mg} = R_{XRF} \cdot \frac{M_{elemental}}{M_{oxide}} \cdot 100\% \tag{4.2}$$

4.2 Optimisation of the agglomeration process

The agglomeration process was optimised using two different 2^2, 5 factor central composite designs (CCD) (Appendix A) with reference to the rotational speed of the disc, the amount of liquid added to the system and the concentration of binders. The response variable was the mass fraction of agglomerates that were in the size range that could be applied to the soil using conventional agricultural spreading equipment (diameter of +2 -5.6 mm), referred to as the yield. The agglomerates of the different binder types in this size fraction are seen in Appendix D. A significant effect of any of

the factors at a confidence level of 95% ($p < 0.05$), would allow for an optimum of that effect to be determined through a surface plot and an ANOVA carried out on the data.

4.2.1 Rotational speed and liquid addition

A 2^2, 5 factor central composite design (CCD) was used to determine if the speed of rotation and volume of liquid addition were significant in the yield of agglomerates produced in the desired size fraction.

The CCD was carried out for sodium alginate and bentonite as binders, where it was assumed that the outcome of these tests could be applied to lignosulphonate. The designed lab-scale agglomerator and screw conveyor, shown in Figure 4.1a were used to produce the agglomerates. Sodium alginate was included as a binder at 2.5% concentration in RO water, where the ratio of bentonite to dry limestone powder was 4:96 g for each bentonite run. The remaining parameters of the runs are described in the CCD shown in Table 4.2, with a detailed experimental design shown in Appendix A.

Table 4.2: Central composite design description of analysis of rotational speed and water addition for sodium alginate (Na-A) at 2.5% concentration and bentonite (B) at 4 g/100g concentration. The yield of agglomerates of +2 -5.6 mm is set as the response variable.

	Coded variables				
	-1.414	-1	0	1	1.414
Na-A - speed [rpm]	20	25	37.5	50	55
Na-A - solution [mℓ]	6	10	20	30	34
B - speed [rpm]	20	25	37.5	50	55
B - RO water [mℓ]	16	20	30	40	44

The sodium alginate solution was made by placing 10 g of sodium alginate powder in a beaker with 400 mℓ of RO water. The beaker was sealed with aluminium foil and stirred with a magnetic stirrer for 30 minutes until fully dissolved. Bentonite was used as a dry binder, where 4 g of bentonite powder was added to 96 g of limestone powder and thoroughly shaken and stirred with a spoon, to ensure homogeneity of the mixture. RO water was used as the liquid for agglomeration with bentonite as a binder, where the amount of liquid that was required for each run is specified in Table 4.2.

The speed of rotation of the disc was set to the speed specified for the run and the amount of water or binder solution specified for the run was placed in a 50 mℓ spray bottle. When the disc reached the set speed, 30 g of the powdered limestone/mixture was placed in the disc. The remainder of the powdered limestone/mixture was placed in the screw conveyor (Figure 4.1b) and added to the disc throughout the run. The binder solution or RO water in the spray bottle was sprayed onto the disc at regular intervals, of approximately 10-20 seconds each, throughout the run. Each run was completed over 30 minutes, where the addition of powder and binder solution or water was continued until all constituents were added to the disc. A 150x50x2 mm metal plate was used as a scraper to ensure that the wet powder did not stick to the face of the disc and that the dry powder was not continuously pressed against the edge of the disc due to the centrifugal forces present in the system. After each 30 minute run, the agglomerates were removed from the agglomerator and dried at room temperature for 24 hours.

After drying, the agglomerates were weighed and sieved with a 5.6 mm and a 2 mm sieve. Those agglomerates that filtered through the 5.6 mm sieve and remained atop the 2 mm sieve, were considered satisfactory in size (in the size range that could be applied using conventional agricultural spreading equipment) and were weighed to determine the yield, the response variable for the run. The unsatisfactory agglomerates were discarded.

This process was repeated for all 9 variations of the CCD, where the centre point run (0,0) was repeated in triplicate. The decoded and detailed CCD experimental designs are shown in Tables A.1 and A.2 for the sodium alginate- and bentonite-limestone agglomerates, respectively. A surface plot was produced using Statistica for each of the binder types and an ANOVA was carried out, with a confidence interval of 95%, on the data to determine the effect that the factors had on the response variable.

4.2.2 Binder concentration and liquid addition

This section discusses the method followed to determine how the binder types (sodium alginate, lignosulphonate and bentonite) and concentration thereof interacts with the amount of liquid added during the agglomeration process. The significance of binder concentration and liquid addition, as well as their interaction, was required to determine if the different agglomerate types needed different volumes of water for an increased yield.

The disc agglomerator (Figure 4.1a) was set to an incline of 45° as recommended by literature. The

speed of rotation was selected as 37.5 rpm, as it was determined insignificant in the range 20 - 55 rpm, from the results of Section 4.2.1. A 2^2, 5 factor CCD, described in Table 4.3, was used to determine if the binder concentration and liquid addition were significant factors on the yield of the agglomerates. A detailed experimental design of the CCD is shown in Tables A.3-A.5.

Sodium alginate and lignosulphonate solutions were both prepared as aqueous solutions with different concentrations and therefore follow the same preparation procedure. Literature showed that fish feed could be produced with appropriate physical properties using a 2% wt/wt sodium alginate solution (Rodriguez-miranda, 2012). The binder was therefore assessed for use in this concentration range, with sodium alginate solutions prepared at concentrations of 1.1%, 1.5%, 2.5%, 3.5% and 3.9% wt/wt with RO water. Lignosulphonate included at 7.5 g/kg in animal feed, were shown to produce a durable product (European Food Safety Authority, 2015). This concentration can be related to 20 mℓ of binder solution with a concentration of 3.75% for 100 g of feed. Lignosulphonate solutions were therefore prepared with concentrations of 2%, 3%, 5%, 7% and 8% wt/wt, as specified in the CCD described in Table 4.3. The solutions were prepared in capped bottles and mixed for 30 minutes using a magnetic stirrer. For these liquid binders, the binder solution was considered the liquid added during process of agglomeration. The production of agglomerates of sodium alginate and lignosulphonate as a binder required 100 g of limestone powder per each run.

Bentonite was however used as a dry binder where the bentonite and limestone powder together made up 100 g of dry powder that was required for this experiment. The dry bentonite-limestone mixture was prepared by adding bentonite to limestone at concentrations of 1-5 g of bentonite per 100 g of bentonite-limestone mixture, with this concentration range recommended by Rychen et al. (2017a). The mixture was shaken vigorously , resulting in 100 g of homogenised bentonite-limestone powdered mixtures. In the bentonite runs - the liquid that was added was RO water, where the volume required for each run is specified for each statistical point in Table 4.3. The liquids required for each run were measured to the volume specified and placed in a 50 mℓ spray bottle prior to starting the agglomeration process.

To begin the agglomeration procedure, 30 g of limestone or bentonite-limestone powder was placed inside the inclined disc. The remaining 70 g was placed in the funnel of the screw conveyor. The motor was switched on and once the disc was rotating at the required speed of 37.5 rpm, the process described in Section 4.2.1 for the production of agglomerates was followed.

After drying, the agglomerates were weighed. They were then sieved at 2 mm and 5.6 mm, where

Table 4.3: Central composite design for analysis of binder (sodium alginate (Na-A), lignosulphonate (LS) and bentonite (B)) inclusion and liquid addition effect on the yield of agglomerates of +2 -5.6 mm in diameter.

	Coded variables				
	-1.414	-1	0	1	1.414
Na-A - binder [%/mℓ]	1.1	1.5	2.5	3.5	3.9
Na-A - solution [mℓ]	6	10	20	30	34
LS - binder [%/mℓ]	2	3	5	7	8
LS - solution [mℓ]	6	10	20	30	34
B - binder [g/100 g]	1	2	3	4	5
B - RO water [mℓ]	16	20	30	40	44

those that were bigger or smaller than the required +2 -5.6 mm were discarded and the mass percentage of the remaining agglomerates was recorded as the response variable for the CCD run.

Statistica was used to produce a surface plot from the data obtained from the CCD and an ANOVA, with a confidence interval of 95%, was carried out to determine the effect that the factors had on the response variable. If a factor had a significant effect ($p < 0.05$), the critical point of the factor was determined by the ANOVA to obtain the binder concentration or the volume of liquid required to maximise the yield.

This section was to obtain the parameters (speed of rotation, liquid inclusion and binder concentration) required to maximise the mass fraction of agglomerates with a diameter in the range, +2 -5.6 mm. The results from these sections were integrated in the production of limestone agglomerates of sodium alginate, lignosulphonate, and bentonite, that were used in the remainder of the research.

4.3 Agglomeration of limestone in a parametrised inclined disc agglomerator

The agglomerates that were produced in this section were used for strength testing to determine which of the binders and concentrations thereof produced agglomerates that could withstand the stresses involved in the processes prior to application. The parameters obtained in Section 4.2 to maximise

the mass fraction of agglomerates produced with a +2 -5.6 mm diameter were implemented in this section. Figure 4.3 is a flow diagram that summarises how the parameters were obtained, what they were, and how they were used in this section. The agglomerator was set to run at 37.5 rpm, from the results obtained from Sub-section 4.2.1. The volume of liquid required to maximise the yield during the agglomeration process was 20 mℓ, 18 mℓ and 22 mℓ for sodium alginate, lignosulphonate and bentonite as binders, respectively (results from Sub-section 4.2.2). Each run to produce agglomerates required 100 g of dry powder - agricultural lime for sodium alginate and lignosulphonate agglomerates and; a bentonite-limestone mixture for bentonite agglomerates.

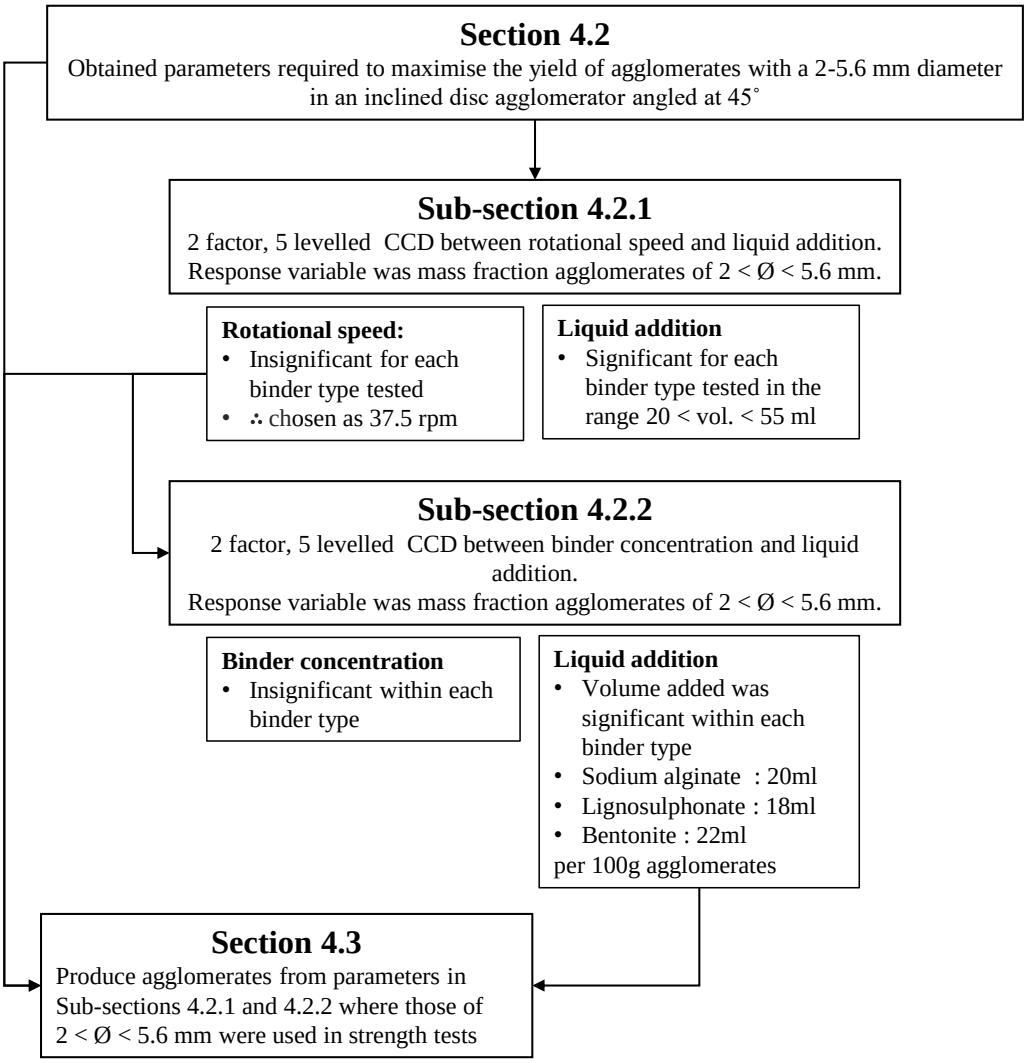


Figure 4.3: A flow-diagram showing how the sub-sections in Section 4.2 were integrated in the production of agglomerates produced for strength tests and further research in this thesis.

Sodium alginate solutions were prepared as liquid binders with concentrations of 0.5%, 1%, 1.5%, 2% and 2.5% in 100 mℓ RO water. In preparation of the solutions, they were placed in capped bottles and stirred on a magnetic stirrer for 30 minutes until the sodium alginate had fully dissolved. For the production of sodium alginate-limestone agglomerates, 100 g of limestone powder was required to make up the dry component of the agglomerate constituents and 20 mℓ of binder solution was placed in the spray bottle as the liquid component. The resulting concentrations of sodium alginate were

therefore 1 g, 2 g, 3 g, 4 g and 5 g per kilogram of limestone, respectively.

Lignosulphonate solutions were also prepared as liquid binders and were therefore prepared using the same method as the sodium alginate solutions. The lignosulphonate solutions were however prepared to have concentrations of 4%, 5%, 6%, 7% and 8% in 100 mℓ RO water. In order to produce agglomerates of each lignosulphonate-limestone concentration, 18 mℓ lignosulphonate solution and 100 g limestone was required. The resulting concentrations of lignosulphonate to limestone powder was therefore 7.2 g/kg, 9 g/kg, 10.8 g/kg, 12.6 g/kg and 14.4 g/kg, respectively.

Bentonite was prepared as a dry binder where the bentonite was mixed into the limestone powder at the concentrations specified, resulting in a total of 100 g bentonite-limestone for each run. Bentonite agglomerates were produced at 1%, 2%, 3%, 4%, 5%, 6% and 7%, where these concentrations were made with 1:99 g, 2:98 g, 3:97 g, 4:96 g, 5:95 g, 6:94 g and 7:93 g bentonite:limestone. These ratios resulted in bentonite/agglomerate concentrations of 10 g/kg, 20 g/kg, 30 g/kg, 40 g/kg, 50 g/kg, 60 g/kg and 70 g/kg, respectively. Table 4.4 summarises the materials used in the production of these agglomerates.

Table 4.4: The liquid addition and binder concentration for each binder type, as well as the binder concentration shown as the corresponding mass of binder required per 1 kg agglomerates to maximise the yield of the agglomeration process.

Binder	Liquid [mℓ]	Concentration prepared	Resulting concentration [g/kg]
Sodium alginate	20	0.5-2.5 [% sol.]	1-5
Lignosulphonate	18	4-8 [% sol.]	7.2-14.4
Bentonite	22	1-7 [%/100 g]	10-70

With the agglomerator set to run at 37.5 rpm, the agglomeration process followed the same procedure to that of Sub-section 4.2.1. After each 30 minute production period, the agglomerates were spread out to a single layer and dried at room temperature for 24 hours, whereafter they were sieved to +2 - 5.6 mm. Those that were too large or too small were discarded, while those that satisfied this size constraint were weighed and stored for strength testing.

4.4 Agglomerate strength tests

The agglomerates of +2 -5.6 mm diameter that were produced in Section 4.3 were used in strength testing in this section. The strength tests were required to determine which of the binder types and concentrations thereof produced agglomerates of a strength that would be appropriate for commercial use. On a commercial scale, agglomerates would have to withstand, being dropped, packaged, packed, stored and transported before being applied to the soil. Testing therefore included an impact test, an abrasion test, a compression test and a moisture disintegration test.

The agglomerates tested were +2 -5.6 mm in diameter and included those of limestone and

- 1 g, 2 g, 3 g, 4 g and 5 g sodium alginate per kilogram agglomerates.
- 7.2 g, 9 g, 10.8 g, 12.6 g and 14.4 g lignosulphonate per kilogram agglomerates.
- 10 g, 20 g, 30 g, 40 g, 50 g, 60 g and 70 g bentonite per kilogram agglomerates.

4.4.1 Drop test

The drop test was adapted from Pietsch (2002) to assess which of the agglomerate types were strong enough to withstand impact forces that they may encounter prior to application to the soil. Industrially produced agglomerates may be exposed to these impact forces on many different occasions, such as when being dropped into storage silos, or poured into packaging.

Figure 4.4 shows the set-up of the drop test. A vertical PVC pipe (3) was designed to a perform the drop test from a height of 1 m. The diameter of the pipe was 50 mm, the recommended 5-10 times smaller than the length (Pietsch, 2002). A collar (2) was placed at the base of the vertical pipe so as to contain the sample after it was dropped. The base (1) of the set-up was chosen as the concrete flooring available in the laboratory where the test was carried out.

Fifteen agglomerates from each of the different agglomerate types were individually dropped from the top of the vertical tube, repeatedly until broken. The number of drops that each agglomerate could withstand prior to breaking was recorded, where "breaking" was defined as the point at which the agglomerate had fractured into two or more parts. The average number of drops that each agglomerate type could withstand prior to breaking was used as a measure of impact resistance.

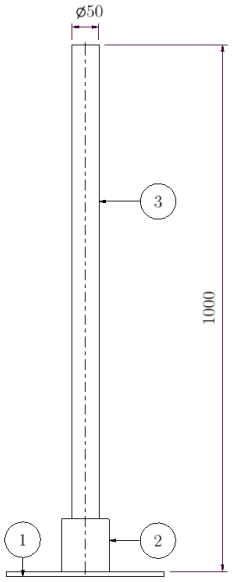


Figure 4.4: A schematic diagram of the designed drop test set up for impact resistance testing. The 1 m tall, 50 mm diameter vertical PVC pipe (3), supported by the collar (2) was set on flat, concrete flooring (1).

4.4.2 Friability test

The friability test was adapted from the pharmaceutical industry, where tablets were tested for resistance against abrasion and attrition (World Health Organization, 2012). On an industrial scale, the agglomerates may be exposed to abrasion when they are packaged, transported, or shifted around in the spreading equipment during application.

The test made use of a shallow cylinder with an inner diameter of 287 mm and a 38 mm deep rim. The cylinder had a baffle with a radius of 80.5 mm fitted from its centre to its rim. The cylinder was fitted to the inclined disc of the agglomerator, where the SEW R17 DT63K4 motor was set to 25 rpm and the inclination angle of the disc was 10° (Figure B.1 in Appendix B). Figure 4.5 shows a front and sectioned drawing of the angled rig used in this test.

Each test consisted of 6.5 ± 0.01 g of an agglomerate type sealed inside the cylinder set to rotate at 25 rpm for 100 rotations or 4 minutes. The agglomerates were weighed prior to testing to obtain the initial mass (IM). After the 100 rotations, the agglomerates were removed from the cylinder and gently hand sieved with a 2 mm sieve to obtain the mass of agglomerates that continued to satisfy the size constraints, this mass was recorded as the final mass (FM). The test was carried out in

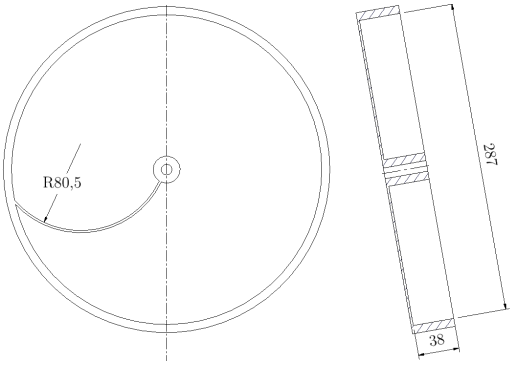


Figure 4.5: A front and sectioned schematic of the rig used in the friability test, designed as per specifications set out by the World Health Organization (2012).

triplicate on each of the agglomerate types where the mass percentage of the agglomerates that turned to powder under abrasion and attrition was calculated as the loss, using Equation 4.3. The average loss experienced by each agglomerate type was used to compare the abrasive resistance of each of the agglomerate types.

$$\text{Loss } [\%] = \frac{\text{IM - FM}}{\text{IM}} \cdot 100\% \tag{4.3}$$

4.4.3 Compression tests

A compression test was carried out on 15 agglomerates of a specific binder and concentration as a proxy for resistance against compressive forces, such as when packages of agglomerates are stored or transported in stock piles. An MTS Criterion 44 Model C Universal Testing Machine was used, set to a maximum compressive load of 700 N. One agglomerate was placed between the two testing plates of the machine at a time, where the load increased at 0.5 mm/minute. TestWorks 4 was used to record the data obtained as the load was increased, where the maximum compressive load that the agglomerate could withstand was extracted using the Python program in Appendix C. The mean maximum compressive force that each of the agglomerate types could withstand was used for comparison of compressive strength that the different binders and concentrations thereof contributed to the agglomerates.

4.4.4 Agglomerate disintegration in water

The time it took for an agglomerate to disintegrate in water was assessed by placing 5 agglomerates per agglomerate type into a 500 mℓ beaker with 120 mℓ RO water. Each agglomerate was timed individually from when the agglomerates were placed in the water until the agglomerates completely lost shape or disintegrated, as determined visually. This process was repeated in triplicate for each of the agglomerate types, where the average time required for the agglomerates to disintegrate was used to compare the resistance to disintegration when the agglomerates were exposed to moisture, such as if rain leaked into a storage silo.

4.4.5 Total strength and desirability

The different agglomerate types underwent the different strength tests in Sub-sections 4.4.1-4.4.4. These tests allowed the agglomerate types to be compared and evaluated based on their different aspects of strength. With this, along with the strength data available in literature, the industrial suitability of these agglomerate types could be evaluated.

A normalised test index was also generated for each strength test in order to easily compare the performance of each of the agglomerate types. The normalised test index (NTI) was calculated for each agglomerate type for each test, using Equation 4.4. The test results (R) from each agglomerate type were normalised according to the highest value achieved across all agglomerate types for that test. The subscript a refers to each agglomerate type, where subscript max refers to the maximum value achieved for each test. The error was adapted to the normalised values, by dividing the it by the maximum result as well. This allowed the strength results to be represented on a scale from zero to one.

$$\text{NTI}_a = \left(\frac{R_a}{R_{max}} \right) \tag{4.4}$$

Suitability of the product for commercial use was also reliant on the cost of the product. The agglomerates were therefore also compared in terms of cost of the agglomerate products, as well as $CaCO_3$, the value product applied to the soil. The April 2020 cost of sodium alginate-, lignosulphonate- and bentonite-powder was \$2600/ton, \$430/ton and \$150/ton, respectively (Alibaba Group Organisation, 2020c,d,a). Micro-fine limestone was estimated at \$142.50/ton (Alibaba Group Organisation, 2020b). Equation 4.5 was used to determine the cost of raw material required per ton of each agglomerate type,

while Equation 4.6 was used to determine the cost of the value product, $CaCO_3$, applied to the soil with each agglomerate type. These equations were used along with the Matlab code in Appendix C. $X_{g/t}$ and $L_{g/t}$ represent the amount, in grams, of binder- and dry limestone-powder required per ton of agglomerates. $\$_X$ and $\$_L$ represents the cost of the binder and limestone as \$/gram. The x represents the quality of the limestone powder, or the fraction of it that is $CaCO_3$, where in this case it is 0.8 ($\approx 80\%$).

The comparison of the cost of the value product considered the difference in concentration of limestone in each of the agglomerate types as a result of different binder concentrations. The different binder types could therefore be compared in strength, as well as how they impacted the cost of both the agglomerates and the value product, $CaCO_3$, that could be applied to the soil. The individual normalised results of the strength tests, were also compared to the cost of the agglomerates and $CaCO_3$ added to the soil, to assess the impact that added strength had on the cost.

$$\$/t \text{ agglomerates} = (X_{g/t} \cdot \$_X \ + \ L_{g/t} \cdot \$_L) \cdot \frac{10^6}{X_{g/t} + L_{g/t}} \tag{4.5}$$

$$\$/t \text{ } CaCO_3 \text{ applied} = (X_{g/t} \cdot \$_X \ + \ L_{g/t} \cdot \$_L) \cdot \frac{10^6}{x \cdot L_{g/t}} \tag{4.6}$$

4.5 Soil lime requirement

In order to determine the amount of limestone that should be applied to the soil to ameliorate soil acidity, a standard lime requirement test was carried out. The Eksteen Method, developed by Eksteen (1969), is used to determine the limestone requirement of soils for various crops in the winter rainfall region, specifically in the South African context. It is based on the ratio between exchangeable calcium and magnesium ($Ca + Mg$) and exchangeable acidity, giving fairly accurate results for the amount of limestone that was to be added to soil in order to increase its pH to a desired level.

Roughly 150 kg of sandy loamy soil was collected from Skilpadsgat farm, Caledon and was dried at room temperature for 72 hours. The soil was sieved to < 2 mm, whereafter it was spread out and homogenised using the cone and quarter method (Horwitz, 1990). The soil that was used in the lime requirement test had the composition described in Table 4.5, as determined from a five fraction analysis by Bemlab (PathCare).

Table 4.5: The composition of the soil used for the lime requirement and in the soil columns.

Soil class	Clay [%]	Sand [%]	Silt [%]	Stone [%]
Fine	19	59	22	0

A 30 g sample of the homogenised < 2 mm soil was weighed out for the lime requirement test. To obtain the exchangeable $Ca + Mg$, a 1N solution of ammonium acetate (NH_4OAc) was required to make a soil solution in a 125 mℓ Erlenmeyer flask. A magnetic stirrer, a Büchner funnel and filter paper were required to carry out the solution preparation.

To obtain the exchangeable acidity of the soil, a titration was to be carried out. A 0.5M K_2SO_4 and a 0.1M KOH solution were prepared, where a burette, a few drops of phenolphthalein indicator and 0.1M NaOH were required to complete the titration.

In order to obtain the exchangeable $Ca + Mg$ required for the Eksteen test, 10 g of < 2 mm air-dried soil was placed in a 125 mℓ Erlenmeyer flask with 40 mℓ of the 1N NH_4OAc solution. The mixture was swirled and left to rest for approximately 1 hour, whereafter it was transferred to a Büchner funnel fitted with a 250 mℓ bottle and a 42 μm pore Whatman filter paper. The remaining grains of soil in the Erlenmeyer flask were transferred to the Büchner funnel with additional 10 mℓ portions of NH_4OAc until there was a total extract volume of 50 mℓ in the suction flask. The filtrate was poured into a 50 mℓ volumetric flask with the additional volume made up by rinsing the suction flask with a fresh 1N NH_4OAc solution.

The resulting solution was filtered again, using a 22 μm pore filter paper. Hereafter, an Inductively Coupled Plasma (ICP) test was carried out to determine the amount of exchangeable Ca^{2+} and Mg^{2+} in the soil. Equation 4.7 shows how Ca^{2+} and Mg^{2+} were converted from the given mg/ℓ (R_{ICP}) to milli-equivalents of cations per litre (meq M^+/ℓ). In order to determine the total exchangeable $Ca + Mg$, the results were adapted to the masses and volumes used in the experiment, where the Ca^{2+} and Mg^{2+} results were added, as per Equation 4.8.

$$\text{meq } M^+/\ell = R_{ICP} \cdot \frac{\text{cation valence}}{\text{cation molecular mass}} \tag{4.7}$$

$$(Ca + Mg)\ \text{cmol.kg}^{-1} = \frac{1}{\text{Soil mass(g)}} \cdot \frac{\text{Extract volume(m}\ell)}{10} \cdot (\text{meq } Ca^{2+}/\ell + \text{meq } Mg^{2+}/\ell) \tag{4.8}$$

The titratable acidity (buffered at pH 7) was also required to determine the lime requirement with the Eksteen test. A 300 mℓ solution of 0.5M K_2SO_4 solution was buffered with 1.5g of CH_3COOK and adjusted to have a pH of 7 using a 0.1M solution of KOH. In a 100 mℓ bottle, 50 mℓ of the pH 7 solution was added to 20 g of < 2 mm air-dried soil. The mixture was stirred for 1 hour and transferred to a Büchner funnel fitted with a 42 μm pore Whatman filter paper. The solution was suction filtered with an additional 150 mℓ of pH 7 K_2SO_4 solution. The filtrate was collected in a 250 mℓ volumetric flask, whereafter 4-5 drops of phenolphthalein indicator was added it. This solution was then titrated with 0.1M NaOH until a permanent pink endpoint was reached.

The titratable acidity (H) was calculated in cmol.kg^{-1} using Equation 4.9. The m_{soil} symbol represents the 0.02 kg mass of soil in the soil solution. The mℓ of NaOH required to reach the pink endpoint was represented as $m\ell_{NaOH}$, with $\ell_{sol.}$ representing the 0.2 ℓ of total soil solution filtered. [$NaOH^+$] represents the 0.1 M molarity of the NaOH used in the titration.

$$H\ [\text{cmol.kg}^{-1}] = \frac{m\ell_{NaOH} \cdot [NaOH^+] \cdot \ell_{sol.}}{10 \cdot m_{soil}} \tag{4.9}$$

The ideal ratio of exchangeable $Ca + Mg$ and titratable acidity (H) is given as the R-value. The amount of $Ca+Mg$ that is required to replace the cmol.kg^{-1} of H^+ to provide a R-value that is suitable for the crop grown, is calculated using the Eksteen method. An ideal R-value of 1.5 is suitable for potatoes and oats; 3 for lupins and wheat; 5 for most vegetables; 10 for fruits and vines and 15 for lucerne (Eksteen, 1969). For research purposes, it is however recommended to use an R-value of 10 to determine a good overall estimate of limestone required in the soil. Equation 4.10 was used to calculate the lime requirement (LR) in tons/hectare of limestone required to rectify the pH of a 15 cm deep profile of soil. R was 10 in this case, with H representing the cmol.kg^{-1} acidity determined with Equation 4.9 and $Ca+Mg$ was the exchangeable calcium and magnesium determined in Equation 4.8.

$$LR\ [\text{t/ha } CaCO_3] = \frac{4[R \cdot H] - (Ca + Mg)}{R + 1} \tag{4.10}$$

4.6 Effect of the agglomerates on a soil profile

Artificial soil columns were used to evaluate the movement of the limestone through the vertical profile of soil.

A test was carried out to determine if the agglomerates would disintegrate when exposed to rainfall or irrigation, allowing the limestone to filter through the soil profile. Six soil columns were designed as per the design considerations set out by Gilbert et al. (2014), where the column diameter was determined by the grain diameter. As the soil had been sieved to 2 mm, the grain diameter was 2 mm. According to Gilbert et al. (2014), the column diameter was to be 40-100 times the grain diameter. Using standard PVC pipe sizes, the pipe diameter was chosen as 200 mm, with an inner diameter of 190 mm. The ratio of column length to column radius should be 4:1, as per the design considerations, resulting in a column height of 400 mm.

Figure 4.6 shows a schematic of the filled soil column, where they were filled using the dry packing method described by Gilbert et al. (2014). The columns were manufactured from PVC pipe with a standard PVC cap attached to seal the base and contain the soil (Figure 4.6). A 360° microjet mist sprayer (BF01) irrigation nozzle (1) was attached to the top, centre of the column to apply water to the system. A tap (4) was placed at the base of the column to allow for drainage of excess water that collected in the column base after filtering through the soil (2). Building stone (3) was washed with RO water and placed in the bottom 10 cm of the column base to prevent soil from being removed from the column along with the excess water.

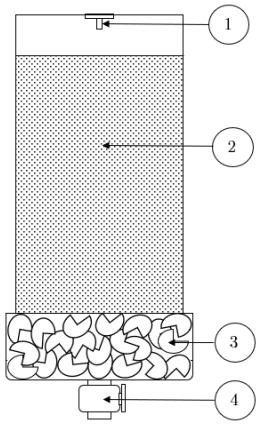


Figure 4.6: A schematic of the soil column, with the nozzle (1), placed above the soil (2). The soil was supported by stones (3) to prevent loss along with run-off water through the tap (4).

With the dry packing technique, the soil was packed from above the stones in 50 mm intervals. After each interval was added to the previous layer, the layer was tightly compacted by hand. In order to avoid stratifications between the layers, the top of each layer was lightly scarified before applying the

next layer. This was repeated for each 50 mm layer until the column was packed to 250 mm with 10.45 kg of soil, resulting in a bulk density of ≈ 1.05 g/cm^3 per column.

The six columns were prepared using the same method, where five of them had limestone agglomerates applied to them and one remained without, to be used as the control. The mass of agglomerates that was applied to each column was determined from the limestone requirement of the soil in Section 4.5. The limestone requirement (LR) of 1.114 t/ha (0.01114 g/cm ^{2}) was adapted for the 283.52 cm^2 surface area (A) of the soil columns. The mass was adapted to cater for the different concentrations (g/ton) of the limestone ($L_{g/t}$) and binder ($X_{g/t}$) in the agglomerates, as per Equation 4.11. Using the calculated 80% of $CaCO_3$ in the limestone, the amount of $CaCO_3$ added through the agglomerates was incorporated into the mass calculation so as to satisfy the lime requirement. Table 4.6 describes each soil column, with reference to the type and amount of limestone agglomerates that were placed on the top soil.

$$\text{mass of agglomerates applied} = \frac{LR \cdot A \cdot (X_{g/t} + L_{g/t})}{0.8 \cdot L_{g/t}} \tag{4.11}$$

Table 4.6: The agglomerates that were selected to be tested in the soil columns and the mass required for each type in order to satisfy the $CaCO_3$ requirement for the soil.

Column	Agglomerate type	Mass agglomerates per column [g]
1	Control	0
2	Sodium alginate [4 g/kg]	3.97
3	Sodium alginate [5 g/kg]	3.97
4	Lignosulphonate [14.4 g/kg]	4.00
5	Bentonite [40 g/kg]	4.11
6	Bentonite [70 g/kg]	4.25

Once the agglomerates were placed on the packed soil columns, each soil column was fitted with the 360° microjet mist-sprayer (BF01) irrigation nozzle (1), as shown in Figure 4.6. The nozzle was fitted to the centre of the opening at the top of the soil column, as well connected to a communal manifold through flexible micro-irrigation pipe of equal lengths. The manifold was attached to a submersible pump in a 20 ℓ drum of RO water. The submersible pump (M) with a head of 10 m is shown in the electrical circuit diagram in Figure 4.7. The electric circuit diagram shows the design for a rain

simulator that was used to apply water to the soil columns at a controlled time and volume, to simulate rainfall through May-July in Malmesbury, South Africa. The circuit included an Arduino® microcontroller and a Real-Time Clock (RTC) run by Arduino® code (Appendix C) to switch the pump (M) on/off to apply water to the soil columns at 3.25 mℓ/s, through the mist-sprayers. The actual circuit and soil columns are shown in Figure B.2 in Appendix B.

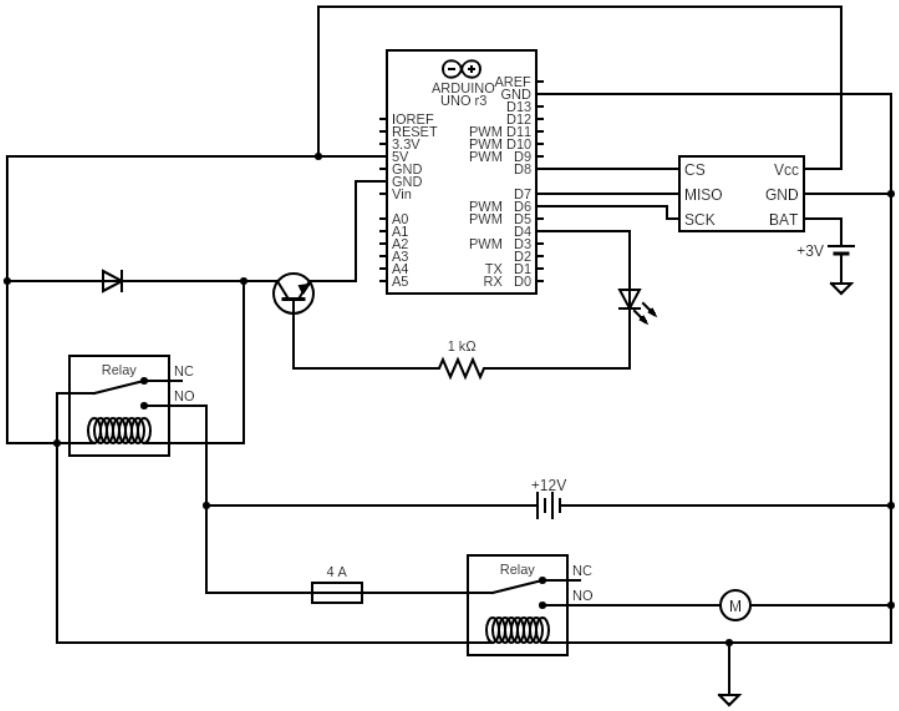


Figure 4.7: The schematic of the automated rainfall simulator used to ensure even water application to the soil columns.

Rainfall data for May-July 2014-2017 in Malmesbury, South Africa was obtained from the South African Weather Services (Appendix E), with an average rainfall of 178.3 mm over the three month period. The three month period in 2015 closely resembled this average, with approximately 174.4 mm rainfall over the period. Therefore, in order to simulate actual rainfall events, the rainfall data from 2015 was used in this simulation. The daily rainfall recorded (in millimetres) for this period was adjusted to a volume of water (millilitres), using the surface area of the columns. Figure 4.8 shows the daily simulated rainfall over the 14-week period.

The soil column experiment was repeated, so that two sets of results were obtained. After each

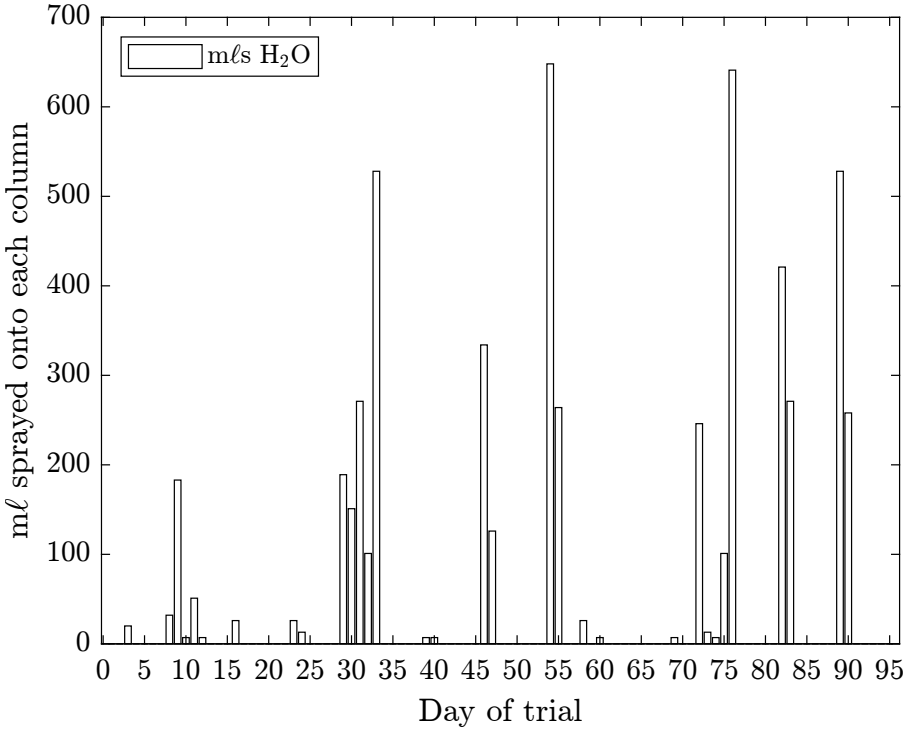


Figure 4.8: The volume of water that is applied to each column in order to simulate the May-July 2015 rainfall.

14-week period of simulated rainfall, each column was sliced into 5, 50 mm segments where each segment represented a region of depth in the soil profile. For the second run of the soil column experiment, the top 0-5 cm of soil was sliced in half to produce a 0-2.5 cm and a 2.5-5 cm segment. This improvement was made so that more detail could be seen in the top soil section, to assess whether or not the micro-fine limestone moved deeper than the surface within the top 5 cm.

The soil segments were broken up and dried at 60°C for 2 hours. Each segment was homogenised using the cone and quarter method (Horwitz, 1990) and stored in sealed containers. Samples were taken from each of the soil segments. Each sample underwent various tests to determine if the agglomerates broke up in the applied water and filtered deeper into the soil profile to allow the limestone to increase the soil pH at depths deeper than the surface.

4.6.1 $CaCO_3$ analysis

A 7 g sample of each of the dried soil segments was collected and placed in a sterilised, labelled container. The samples were sent to the Central Analytical Facilities (CAF) of Stellenbosch University where they underwent XRF analysis. The XRF analysis provided the chemical composition of the soil, where CaO was one of the results obtained (CaO_{XRF}). Again, it was assumed that CaO was bound to CO_2 as $CaCO_3$. Therefore, once again, using the molecular masses (M) of CaO and $CaCO_3$, with Equation 4.1, the value of CaO was converted to amount of $CaCO_3$ in the soil sample.

$$\%_{\mathrm{CaCO_3}} = \mathrm{CaO}_{XRF} \cdot \frac{\mathrm{M}_{\mathrm{CaCO_3}}}{\mathrm{M}_{\mathrm{CaO}}} \cdot 100\% \tag{4.1}$$

4.6.2 pH analysis

The pH of the soil segments were measured using the method described by Eksteen (1969). A 1M potassium chloride (KCl) solution was prepared by placing 74.55 g KCl into 1 ℓ of RO water. The solution was stirred in a capped bottle for 30 minutes using a magnetic stirrer.

Ten grams of soil was placed in a 50 mℓ centrifuge tube. A calibrated pipette was used to add 25 mℓ of the 1M KCl solution to the 10 g of soil. The suspension was mixed on a rotating mixer at room temperature for 1 hour. Hereafter, the pH was measured in triplicate using a calibrated Hanna pH meter.

4.6.3 Electrical conductivity analysis

An RS 180-7127 hand-held conductivity meter with a resolution of 0.1 μS and accuracy of ±6% was used to measure the electrical conductivity (EC) of each soil sample. The meter was calibrated as per the manufacturer's instructions using a KCl reference solution. The reference solution was made up using 0.746 g KCl added to 1 ℓ RO water (0.1 M KCl). The solution was stirred with a magnetic stirrer for 30 minutes, resulting in a solution with an electrical conductivity of 1.413 mS/cm. The meter was calibrated using this solution.

The EC of the different soil segments was analysed with the use of the calibrated EC meter. A 1:5 soil:RO water suspension was made by weighing and adding 5 g of air-dried < 2 mm soil from each column segment to 25 mℓ of RO water. The solution was prepared in 50 mℓ centrifuge tubes and

mixed on a rotating mixer for 1 hour in order to dissolve the soluble salts. The calibrated meter was placed in the suspension and a reading was taken in triplicate for each soil sample.

4.7 Summary

An inclined disc agglomerator was designed and manufactured as per specifications set out by Capes (1980). The agglomerator was used in the agglomeration of limestone with sodium alginate, lignosulphonate and bentonite used as different binders. The significance of, (1) speed of rotation of the disc, (2) the volume of liquid added to the system and (3) the concentration of binder, was assessed in order to maximise the mass fraction of agglomerates in the +2 -5.6 mm diameter range (yield). It was found that speed of rotation had an insignificant effect on the yield in the 20-55 rpm range and the agglomerator could be set to 37.5 rpm. The volume of liquid added to the system had a significant influence on the yield for each of the binder types. Agglomerates were then produced in 100 g batches, with 20 mℓ and 18 mℓ of binder solution for sodium alginate- and lignosulphonate-limestone agglomerates, respectively. Bentonite-limestone agglomerates were produced with 22 mℓ RO water. These agglomerates underwent strength tests, as a proxy for resistance to breakage on impact, under abrasive and compressive stress and in the presence of moisture.

A lime requirement was carried out on soil obtained from Caledon, South Africa. The Eksteen lime requirement test was used as it is the appropriate method for South African soils. Agglomerates of each binder type were selected and placed on the surface of artificial soil columns in masses corresponding to the lime requirement. The soil columns underwent a 14-week rain simulation, automated with the use of an Arduino®. After the 14-week period, the soil columns were segmented at different depths, where samples from each segment underwent XRF analysis, and pH and EC testing. This was to determine if there was an increase in $CaCO_3$ or pH at levels lower than the surface.

Chapter 5

Results and discussions

5.1 Introduction

This chapter discusses the results that were obtained from the methods followed in Chapter 4. Much of this work has been published in "The effect of sodium alginate, lignosulfonate, and bentonite binders on agglomeration performance and mechanical strength of micro-fine agricultural lime pellets" by Schwaeble, Pott, and Goosen (2020).

The designed agglomerator and the agglomeration process was assessed with the use of two, 2^2, 5-factor CCDs to maximise the yield of agglomerates produced in the +2 -5.6 mm diameter range. The agglomerates in the correct size range that were produced using the findings from the CCDs underwent strength testing to compare how the different binder types and concentrations thereof effected the resistance to impact, attrition, compression, and moisture degradation. A lime requirement test was carried out, where a specific mass of agglomerates that were proven of the strongest for each of the binder types, were placed on the surface of artificial soil columns. The columns were exposed to a 14-week rainfall simulation to determine if the different limestone agglomerates could ameliorate soil acidity at depths deeper than the surface after their application.

The results gave insight into the industrial viability of the micro-fine limestone agglomerates in terms of mechanical strength, cost, and achieving their goal of treating soil acidity.

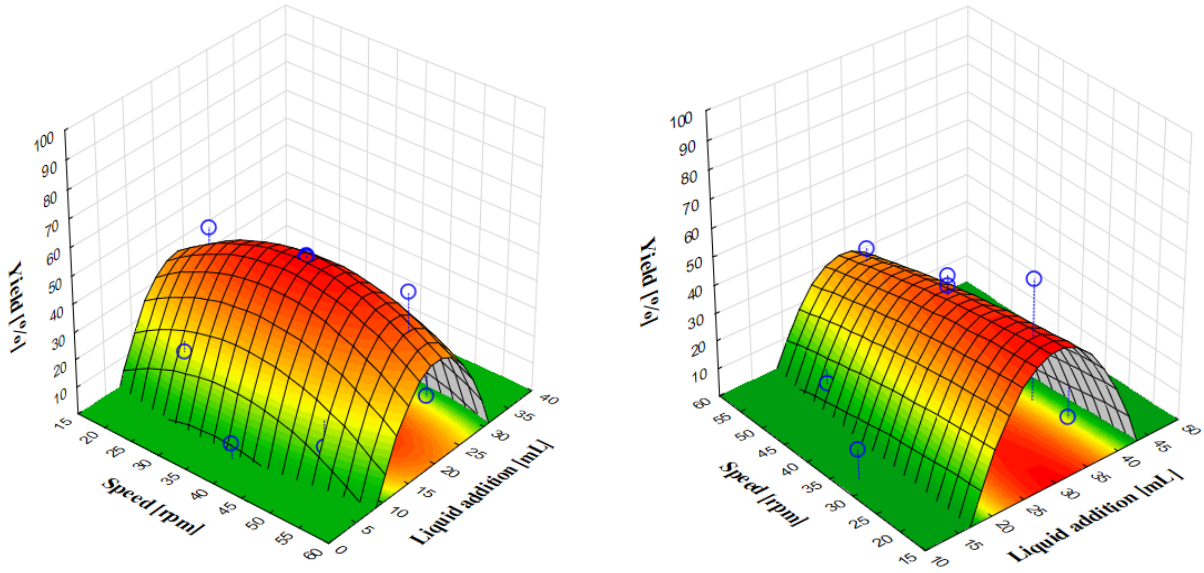
5.2 Optimisation of the Agglomeration process

It was important to maximise the yield of agglomerates of +2 -5.6 mm diameter produced in each run. Agglomerates of that size were considered preferable as they would be of a similar size to commonly used fertilisers and can therefore be spread with conventional agricultural spreading equipment. Many

factors have an influence on the agglomeration processes, but speed of rotation, liquid inclusion and binder concentration were evaluated in this section.

5.2.1 Rotational speed and liquid addition

Two factors, namely rotational speed of the inclined disc and liquid addition, of the agglomeration process were assessed with mass fraction of agglomerates between +2 -5.6 mm diameter (the yield) set as the response variable. The process was evaluated for the production of agglomerates with a 2.5% wt/wt sodium alginate binder solution, as well as a 4:96 g bentonite-limestone mixture. A 2^2 CCD was used to determine the significance of speed of rotation and liquid addition, where the results are presented as surface plots in Figure 5.1.



(a) Sodium alginate included as a 2.5% solution.

(b) Bentonite included at 4% in the powdered mixture.

Figure 5.1: A surface plot of the yield obtained through the CCD analysis of the rotational speed of the agglomerator and binder solution (a), or water (b) added to the system. The plots have an R^2 of 0.86 (a) and 0.74 (b) with the regression equations shown in Appendix G.

At insufficient speeds the powdered materials would remain at rest during rotation of the disc, whereas at excessive speeds the centrifugal forces in the system prevent the rolling of the materials and in turn

prevent agglomeration (Pandey, Lobo, and Kumar, 2012). However, in the range tested, the speed of rotation did not have a significant impact ($p > 0.05$) on the formation of agglomerates. The volume of binder solution or water added to the system did however have a significant impact ($p < 0.05$) on the size of the agglomerates that formed. The interaction between the speed of rotation and the volume of liquid that was added to the systems was also insignificant ($p > 0.05$), as determined by the ANOVA at a 95% confidence interval. The quadratic equations for the surface plots are given in Appendix G, with R^2 values of 0.86 (a) and 0.74 (b), indicating that the data fit the plot relatively well. Figure 5.1 can be used to visualise the results from the ANOVA, where the curved line at the *liquid addition* axis indicates that there was a tighter range of liquid that could be added to the system, whereas the more straight lines parallel to the *speed* axis show that this tighter range of liquid applied to most of the speeds tested. This supports the notion that the formation of agglomerates is primarily dependent on the moisture content during formation of the product (Pandey, Lobo, and Kumar, 2012).

If moisture were more than the critical amount, the agglomerates would have grown too large and would have been prone to deformation due to increased plasticity. When moisture was below the critical amount, its distribution was relatively non-uniform, leaving large quantities of materials in powder form. Figure 5.1a shows that 2.5% sodium alginate:water solution should have been included in the range of 15-25 mℓ for 100 g of limestone powder to maximise the yield. The surface plot in Figure 5.1b shows that for a bentonite-limestone mixture of 4:96 g, the water should be added in the range of 20-40 mℓ. The significance of liquid addition and the insignificance of speed of rotation was assumed applicable for lignosulphonate as binder. Although the significance of liquid addition was determined in this section, the volume required to maximise the mass fraction of agglomerates of +2 -5.6 mm for each binder type and concentration thereof was to be determined.

5.2.2 Binder concentration and liquid addition

As determined in Sub-section 5.2.1, liquid addition had a significant impact on the formation of agglomerates. The moisture content should not have been less or more than the required amount, as this would have either left excess powdered material, or agglomerates that were too large (Pandey, Lobo, and Kumar, 2012; Jacob et al., 2019).

In order to determine the liquid requirement of each of the binders, it was required to determine if volume of liquid added and binder concentration were independent of one another and if they influence the yield of +2 -5.6 mm agglomerates. A 2^2, 5 factor CCD was carried out for each of the

three different binder types, namely sodium alginate, lignosulphonate and bentonite. The binder types were tested at various binder concentrations and with different volumes of liquid added to the system. The response variable of the CCD was the yield of +2 -5.6 mm agglomerates. Surface plots of the resulting data were limited to regions with positive values for the yield and are shown in Figures 5.2-5.4. With an ANOVA carried out on the CCD results from each binder type, the binder concentration was determined to be insignificant ($p > 0.05$), whereas volume of binder solution or water added was determined as significant ($p < 0.05$). The interaction effect between the binder concentrations and the volume of liquid added was also found to be insignificant ($p > 0.05$). The critical volume of liquid required to maximise the yield could therefore be determined for each binder type from the data obtained in the CCDs. The results relating to each of the binder types were discussed individually in more detail. Figure 5.2 shows the surface response of the CCD analysis described by Table 4.3, with respect to sodium alginate used as a binder.

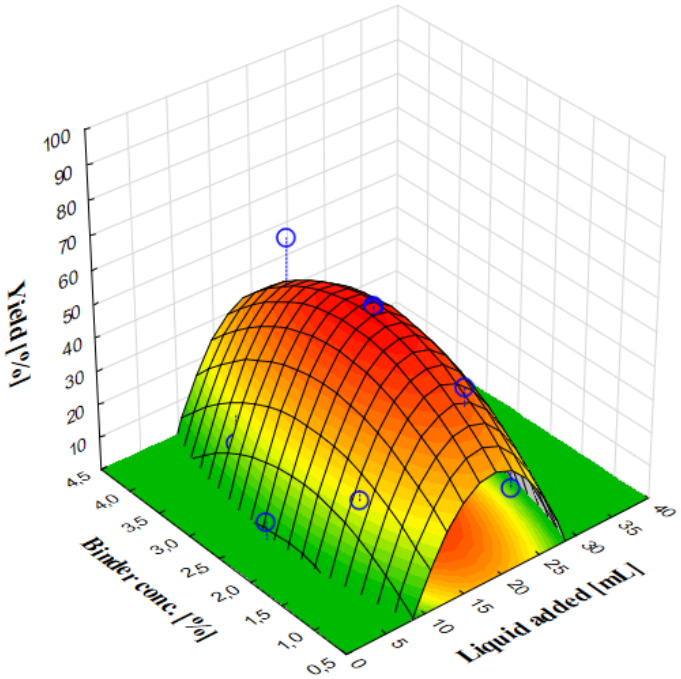


Figure 5.2: Surface plot for the yield response (corrected for yield > 0) to various concentrations of sodium alginate and volumes of binder solution added. Yield response was the percentage of agglomerates between +2 -5.6 mm. At 20 mℓ liquid inclusion the estimated yield was 53.1% for 100 g limestone powder.

The surface plot in Figure 5.2, with the equation shown in Appendix G, had an R^2 of 0.87. The data therefore fit the plot relatively well. An ANOVA with a confidence interval of 95% was carried out on the results and it was determined that there was a strong quadratic relationship between the yield and the volume of sodium alginate solution added to the system ($p < 0.05$). The results showed that the concentration of the binder, as well as its interaction with the volume of solution, did not have a significant impact on the yield of well-sized agglomerates ($p > 0.05$). This relationship showed that the optimal amount of sodium alginate solution added to this system was 20 mℓ per 100 g limestone powder, regardless of the concentration of the solution. With 20 mℓ of sodium alginate solution added to 100 g of limestone powder, an approximate yield of 53.1% was predicted. When too little sodium alginate solution was added to the system, the calcium ions in the calcium carbonate or limestone reacted with the available sodium alginate polymers, forming a hardened outer layer on the forming agglomerate. Due to the insufficient amount of liquid and a finite amount of powder, the hardened layer was not re-coated with an adhesive layer, inhibiting further growth of the agglomerate. This lead to majority of the agglomerates that were produced to be too small to satisfy the lower size requirement of the product. When liquid addition exceeded the 20 mℓ, the agglomerates were coated with additional adhesive layers of sodium alginate solution. These added layers caused the larger agglomerates to attach to one another, resulting in agglomerates that were too large to satisfy the size requirements of the product.

As with sodium alginate, lignosulphonate was applied as a liquid binder solution. Figure 5.3 shows how the concentration of this liquid solution, as well as how the volume thereof, impacted the yield of agglomerates produced during each process. The plot had an R^2 of 0.42, indicating that the data did not fit the plot particularly well, which could be explained by the large variability seen in the plot. This variability was a result of additional runs at different statistical points in the CCD for an increased yield. The statistical points of the standard 2^2, 5 factor CCD described for lignosulphonate in Table 4.3 gave relatively low yields of approximately 20% per run, therefore 2 repeats of three additional runs were added to the analysis (as seen in Table A.4 in Appendix A). Eighteen millilitres (or -0.2 as a statistical point) was estimated as an intermediate point to potentially result in a higher yield. This volume of binder solution was tested at lignosulphonate concentrations of 4%, 5% and 7% (statistical point -0.5, 0 and 1 respectfully). The yields obtained at 18 mℓ were approximately 30% higher than of that recorded at other points, explaining the large variability seen in the plotted surface response. An ANOVA carried out on the 17 runs showed that lignosulphonate had a similar result to that of sodium alginate in that the concentration of the binder was not significant ($p > 0.05$) in the size of the

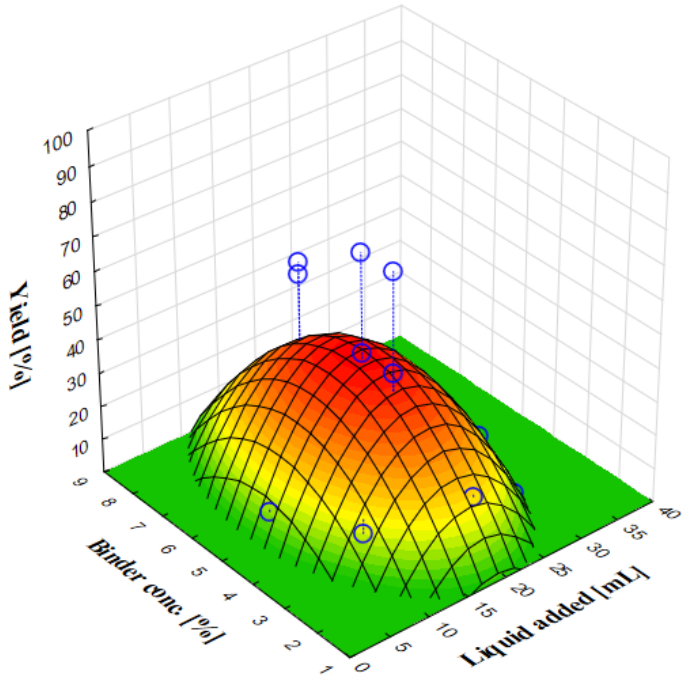


Figure 5.3: Surface plot corrected for the yield response (corrected for yield > 0) to various concentrations of lignosulphonate and volume of binder solution added. The high variability seen was owed to an increased yield (agglomerates of +2 -5.6 mm diameter), at the additional points, 18 mℓ liquid addition at various concentrations, compared to that of the other volumes of liquid addition tested. The surface plot predicts a yield of 41% at 18 mℓ liquid addition.

agglomerates that formed, but rather that the amount of lignosulphonate solution that was added to the system was significant in the formation of agglomerates of the required size ($p < 0.05$). The critical values obtained from the statistical analysis suggested that $\approx$ 18 mℓ of lignosulphonate solution was the critical amount of solution that should be added for 100 g limestone powder, where a yield of 41% was predicted.

Figure 5.4 shows the surface plot that resulted from the data obtained from the CCD analysis described in Table 4.3, for bentonite as a binder. The plot was limited to have a yield of 0-100%, irrespective of the regression equation - emphasising the curve of the graph. The data obtained in the CCD fitted the resulting equation for the surface plot relatively well, with an R^2 of 0.88 (Appendix G).

Bentonite was used as a dry powder, where it was homogenised with the limestone powder to produce a bentonite-limestone mixture. RO water was added to the system during agglomeration. An ANOVA

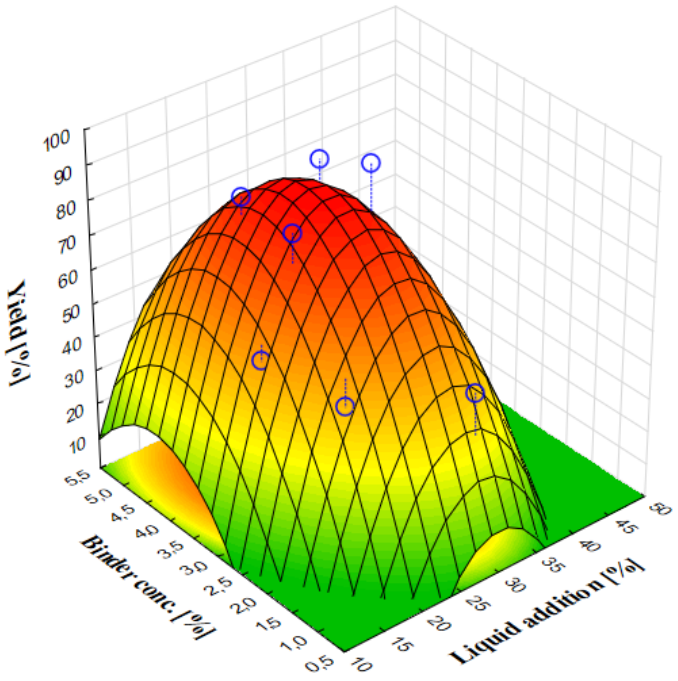


Figure 5.4: Surface plot for the yield response to various concentrations of bentonite and volumes of RO water added. Plot limited to yields > 0.

with a 95% confidence interval was carried out on the data obtained, and showed that the amount of bentonite added to the limestone powder was insignificant ($p > 0.05$) with respect to agglomerate size, whereas the volume of water added was significant ($p < 0.05$). The interaction of these two factors was also shown to be insignificant ($p > 0.05$) on the resulting agglomerate size. Figure 5.4 shows that $\approx$ 22 mℓ of water per 100 g of bentonite-limestone mixture was the critical amount required to maximise the yield. With this, an estimated yield of 90.3% was predicted, which was high compared to that of sodium alginate and lignosulphonate.

In the presence of water, the swelling nature of bentonite allowed the forming agglomerates to swell, increasing their volume and surface area. This allowed for the adsorption of more powdered materials, further increasing the size of the agglomerates. When the system was saturated with water, excessive swelling and adsorption took place. The additional growth set the agglomerates out of the size limits, decreasing the yield of the usable agglomerates. Too little water had the opposite effect, where the agglomerates could not adsorb enough additional bentonite-limestone powder and were too small to satisfy the size requirements when dried. These results showed that the amount of liquid that was added to the system was the primary factor influencing the formation of agglomerates, agreeing with

what is stated in literature (Pandey, Lobo, and Kumar, 2012). Green and Perry (2008) state that 29.5-32.1 wt% of moisture is required to produce a balled product of precipitated calcium carbonate with a particle size of < 200 μm as the raw material. The limestone used in the source was approximately 5 times larger than that of this section. Due to increased surface area with the use of finer limestone, stronger inter-particle forces required less moisture for bonding, therefore the moisture content of approximately 20 wt% was considered to agree with what is stated in literature.

Although binder concentration was not an influencing factor on the size of the agglomerates, it may have had an impact on their strength, which was determined in Section 5.4 of this research. The results from this section were implemented in the production of agglomerates of different binder types and binder concentrations in Section 5.3, where the products were used in the strength tests.

5.3 Agglomeration of limestone in a parametrised inclined disc agglomerator

The agglomerates that were produced in this section were produced using the results from Subsections 5.2.1 and 5.2.2. The designed agglomerator was therefore optimised for a maximised yield of +2 -5.6 mm agglomerates. The agglomerator did not have a feedback system where agglomerates that did not satisfy the lower size limit could be fed back into the system in order to maximise yields, this could however be implemented in an industrial scale disc agglomerator. Figure 5.5 shows the yield of agglomerates of a diameter (∅) in the +2 -5.6 mm range for each type of agglomerate produced.

The figure shows that the different binder concentrations of sodium alginate had similar yields, with an average yield of ≈ 40.5%. Although this was a relatively low yield, with feedback of smaller agglomerates in an industrial scale agglomerator it is likely to be higher. As sodium alginate formed cross-linked bonds with the calcium ions in the limestone powder, granules formed when the solution and the limestone powder came into contact. The viscous nature of the binder therefore results in larger droplets of solution as it was sprayed onto the system. More limestone was therefore initially encapsulated by the sodium alginate droplets and resulted in larger granules. These granules produced larger agglomerates than that of the less viscous lignosulphonate solution and water, added in the production of lignosulphonate- and bentonite-limestone agglomerates, respectively. Although viscosity can be considered in an additional study, it is important to note that this result was an indication that the predicted yield of 53.1%, made by the surface plot in Figure 5.2 was relatively accurate in that it

was not significantly high.

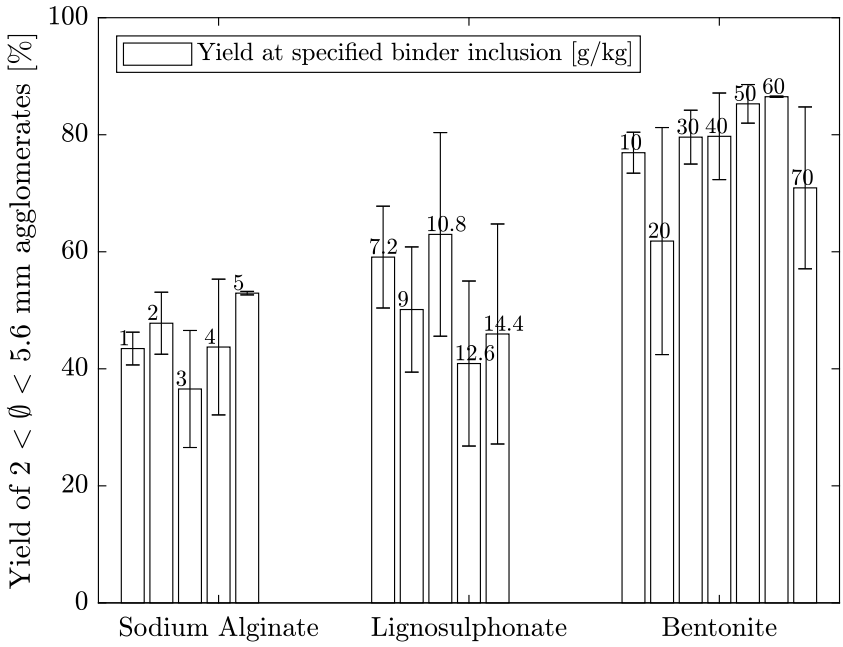


Figure 5.5: The average mass fraction of agglomerates in the required diameter range for the different binder types, where the binder concentration is specified (in grams of binder per kilogram agglomerates) above each bar.

Figure 5.5 shows that agglomerates produced with lignosulphonate used as a binder at different concentrations had an average yield of 51.8% using the parameters specified in Section 4.3. Lignosulphonate relies on the sticky properties of the solution to bond particles, rather than cross-linking bonds between particles. The lignosulphonate solutions were less viscous than that of sodium alginate, where the lignosulphonate solution could settle between the finer limestone particles to form smaller granule nuclei. These smaller nuclei could increase in size relatively uniformly, allowing for a slightly smaller size distribution of the product. The yield of lignosulphonate-bonded agglomerates produced in this section was 10% more than the yield of 41% predicted in Sub-section 5.2.2. It was however a relatively accurate prediction in that the agglomerates produced at 18 mℓ liquid inclusion in Sub-section 5.2.2, had yields in the region of 50%. The average yields of the different concentrations of lignosulphonate-bonded agglomerates agglomerated with 18 mℓ of binder solution, shown in Figure 5.5, were also in a similar region and do not follow a specific trend. This reiterates that

the binder concentration had little impact on the outcome of the agglomerates - supporting what was stated in Sub-section 5.2.2.

The average yield for the bentonite-limestone agglomerates was 75.3%. This was high compared to the other two binder types, and can be considered in line with the high yield of 90% predicted in Sub-section 5.2.2. This was owed to the homogenised bentonite-limestone mixture, where when wetted, the bentonite could adsorbed the water as well as the surrounding limestone, producing product with a relatively tight size distribution. Figure 5.5 shows no relationship between the yield of well-sized agglomerates and the concentration of bentonite in the mixture, supporting the results in Sub-section 5.2.2 that the bentonite concentration does not have a significant impact on the size of the agglomerates produced.

The agglomerates that were produced in this section and deemed acceptable in size were stored in a dry environment for further experimental use, including strength testing.

5.4 Agglomerate strength tests

The procedure for the strength tests were discussed in Section 4.4. Testing included a drop (impact) test, a friability test, a compression test and a moisture disintegration test. These tests were used to compare the strength and resistance to breaking of the agglomerates of different binder types and concentrations. The detailed results of each of the strength tests are shown in Appendix H.

5.4.1 Drop test

The drop test was carried out as a proxy for agglomerate resistance to breakage when exposed to impact forces. It entailed repeatedly dropping 15 agglomerates of each agglomerate type from a height of 1 m until broken. The average number of drops survived by each agglomerate type is shown in Figure 5.6.

In order to resist breaking prior to application to the field, a stronger agglomerate was preferred. This can be related to an agglomerate that resisted breaking for more drops in the drop test. There is a lack of literature data for uncoated agglomerates of the size investigated, therefore an absolute number of drops that an uncoated agglomerate should survive would need to be determined *in situ*. Regardless, these tests offer insight into the relative strength added through the use of the different binders.

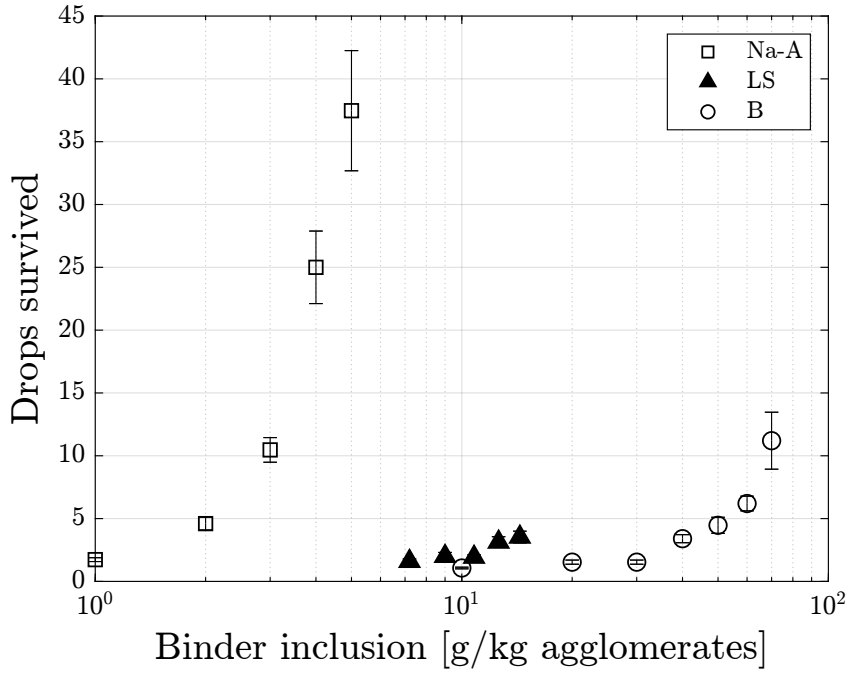


Figure 5.6: The average number of drops survived by agglomerates of different binder types, sodium alginate (□), lignosulphonate (▲) and bentonite (○) when dropped from a height of 1 m in an impact strength test.

The linear-log graph, Figure 5.6, shows a clear increase in the number of drops survived as the binder concentration increases for each binder type. The increase in number of drops survived was related to an increase in strength as a result of an increase in binder concentration. The agglomerates were therefore more resistant to breakage when exposed to impact stresses at higher concentrations of binder. The agglomerates will typically experience impact stresses throughout the packaging process and the loading of transportation vessels and storage silos (Pietsch, 2002).

Sodium alginate performed the best in comparison to lignosulphonate and bentonite, even though very low concentrations of binder were included. One gram of sodium alginate binder was expected to contribute ±9.18 drops, whereas 1 g of lignosulphonate and bentonite contribute ±0.27 and ±0.15, drops respectively. Therefore, supporting Figure 5.6, sodium alginate was more effective as a binder to produce a product that was resistant to breakage on impact compared to the other two binders. At higher concentrations bentonite showed an increase in impact resistance, however it performed poorly at concentrations less than 60 g/kg.

Sodium alginate relies on cross-linking of ions in the formation of strong bonds between that of the binder polymers and the calcium ions in the limestone. This bond may be more resistant to breakage on impact compared to the lignosulphonate- and bentonite-bonded agglomerates that rely on the adhesive properties from adsorption (Clem and Doehler, 1961; Nedosvitii et al., 1994; Russo, Malinconico, and Santagata, 2007). The impact resistance may also be owed to the physical properties of the agglomerates. Sodium alginate as a binder produced smooth, oval agglomerates, where those of lignosulphonate and bentonite were of irregular shapes with some having pointed edges. These edges create weak lines in the product which easily break off upon impact. The smooth surface of the sodium alginate agglomerates could therefore have been a contributing factor to its performance in the drop test.

To compare the agglomerates to one another, those agglomerates that could withstand more than the average of 7 drops were considered preferable over those that did not. These include ≥3 g sodium alginate and 70 g bentonite per kilogram of agglomerates.

5.4.2 Friability test

The results from the friability test give an indication of how resistant the agglomerates are to abrasive wear. The results from the test are shown in the linear-log graph in Figure 5.7, where a large result indicated large losses, suggesting low resistance to abrasive wear.

Figure 5.7 shows a negative relationship between the binder concentration and the loss that the agglomerates experience, therefore as the concentration of sodium alginate, lignosulphonate or bentonite increased in the agglomerate, it experienced less loss. The lower concentrations of each of the binder types fared poorly with losses over 30%, whereas at higher concentrations all the binder types had improved resistance to breakage and generally experienced less than 10% of loss. There was a slight increase in the loss at 5 g sodium alginate and 14.4 g lignosulphonate per kilogram agglomerates, which may be owed to crusts of binder that coated the agglomerate that were sloughed off with the abrasion.

Bentonite experienced a steady decrease in loss with the increase in binder concentration, where each gram of bentonite added, contributed to an estimated resistance to loss of ±1.15%. Although the linear-log representation of the data does not make it clear, a gram of sodium alginate and lignosulphonate provided an estimated resistance of ±6% and ±2%, respectively. Therefore, as individual binders, sodium alginate performed the best as a binder compared to that of lignosulphonate and

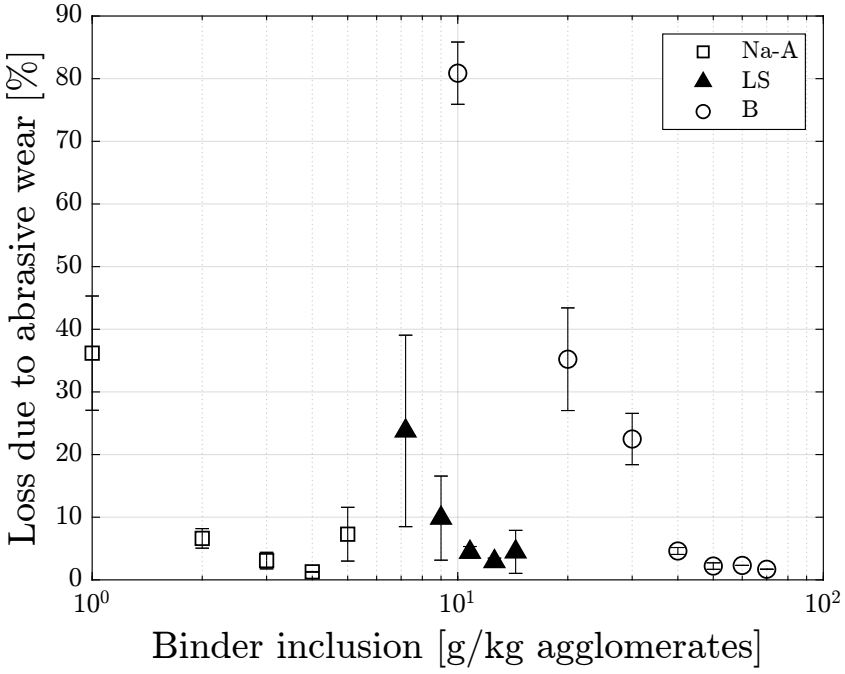


Figure 5.7: The mass percentage of loss experienced by agglomerates of different binders after 6.5 g of whole agglomerates were rotated in a cylinder at 25 rpm for 100 rotations. Symbols: □, sodium alginate; ▲, lignosulphonate; and ∘, bentonite.

bentonite, which performed competitively with one another.

Most fertilisers suffer a 0.4-21% degradation during mass abrasion resistance tests (Rutland, 1986) For this test used in the pharmaceutical industry, the standard only allows for a maximum degradation of 1% for pharmaceutical tablets (World Health Organization, 2012). Although the absolute acceptable loss is to be determined *in situ*, with these sources considered, agglomerates that exhibited a friability loss of < 5% were considered to perform acceptably in resisting abrasive wear. With this considered, agglomerates of i) 3-5 g sodium alginate, ii) 9-14.4 g lignosulphonate, and iii) 40-70 g bentonite per kilogram were considered to perform acceptably in the resistance of abrasive wear.

5.4.3 Compression test

Figure 5.8 shows the maximum force that each of the agglomerates could withstand when exposed to an increasing compressive force.

During the compression of spherical agglomerates, the particle-particle bonds fail locally as flattening

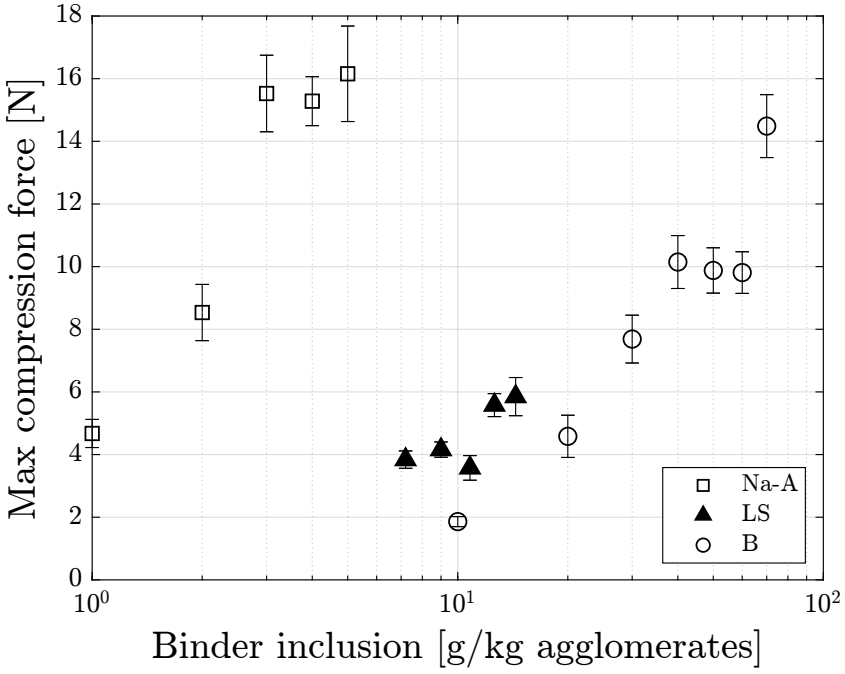


Figure 5.8: The maximum compressive force agglomerates of different binder types and concentrations can withstand when exposed to an compressive load increasing at 0.5 mm/minute. Symbols: □, sodium alginate; ▲, lignosulphonate; and ∘, bentonite

of the agglomerate occurs. The particles are then forced into contiguous voids, where the shift causes small dense regions against the faces of the compression rig. These dense regions cause the agglomerate to fail under tension along a circumferential crack that joins the loaded poles (Pietsch, 2002). The agglomerates that could experience more compressive force while remaining intact, required more force for these dense regions to form and were therefore more resistant to cracking.

The results in Figure 5.8 show that there was a strong positive correlation between the maximum compressive force that an agglomerate could withstand and the concentration of a specific binder. The figure shows that sodium alginate could resist breakage at much higher forces compared to that of the majority of the bentonite- and lignosulphonate-limestone agglomerates. With this considered, a gram of sodium alginate contributed ±3 N of compressive strength, whereas lignosulphonate and bentonite only contributed ±0.3 N and ±0.18 N per gram of binder, respectively. Sodium alginate was therefore responsible for approximately 10 times the strength per 1 g of binder when compared to lignosulphonate and bentonite, which were once again competitive with one another.

In the region of lignosulphonate concentration tested, it appeared that lignosulphonate performed better than bentonite at similar concentrations. With the strength contribution of ±0.3 N per gram lignosulphonate, this is expected to be the case at higher concentrations of lignosulphonate and bentonite as well. However, at the concentrations tested, lignosulphonate was not competitive in compressive strength when compared to > 3 g sodium alginate and > 40 g bentonite per kilogram agglomerates.

As mentioned, sodium alginate performed far better than the other binders at far lower concentrations. This was owed to the strong bonds that formed between the sodium alginate polymers and the calcium ions during agglomeration. The cross linking that occurred may have prevented the particles from moving and forming dense voids at the faces of the rig, allowing the agglomerates to resist cracking under increased loads. Sodium alginate employed a chemical mechanism for bonding, whereas lignosulphonate and bentonite relied on a weaker, adsorption method for bonding. This explains how they performed competitively with one another at similar binder concentrations and poorly in comparison to sodium alginate at lower concentrations, supporting the results obtained in the drop test (Sub-section 5.4.1).

An absolute minimum compressive force required for uncoated agglomerates of this size needs to be determined *in situ*. However, the crushing strength of common fertilisers range from 7.8-40 N, where those of 2.36-2.80 mm should withstand a minimum crushing force of 14.7 N (United Nations Industrial Development Organization and International Fertilizer Development Organization, 1998). Exceeding this minimum crushing force, agglomerates with concentrations of 3-5 g sodium alginate and 70 g bentonite per kilogram, proved to be competitive with what is stated in literature.

5.4.4 Agglomeration disintegration in water

This test was developed as a method to compare binder types and concentrations with regards to the time taken for the agglomerate to disintegrate when fully immersed in water. This is an important factor to consider when the purpose of the limestone is for it to penetrate further into the soil than where it is applied, so as to increase the pH of the soils at levels deeper than the surface, such as the root zone of the crop. The agglomerates are therefore expected to disintegrate when exposed to water, such as in rain- or irrigative-water, allowing the limestone particles to be transported through the soil profile. The agglomerates that resisted disintegration for longer during this test indicated that they will disintegrate only when saturated in the field, rather than when exposed to small amounts of moisture, e.g. during transportation, storage, or handling.

Figure 5.9 is a graphical display of the time taken by each of the agglomerates to lose shape, as determined visually, during the moisture disintegration test. The positive relationship seen in the graph makes it clear that the agglomerates were more resistant to moisture disintegration as binder concentration increased for each binder type.

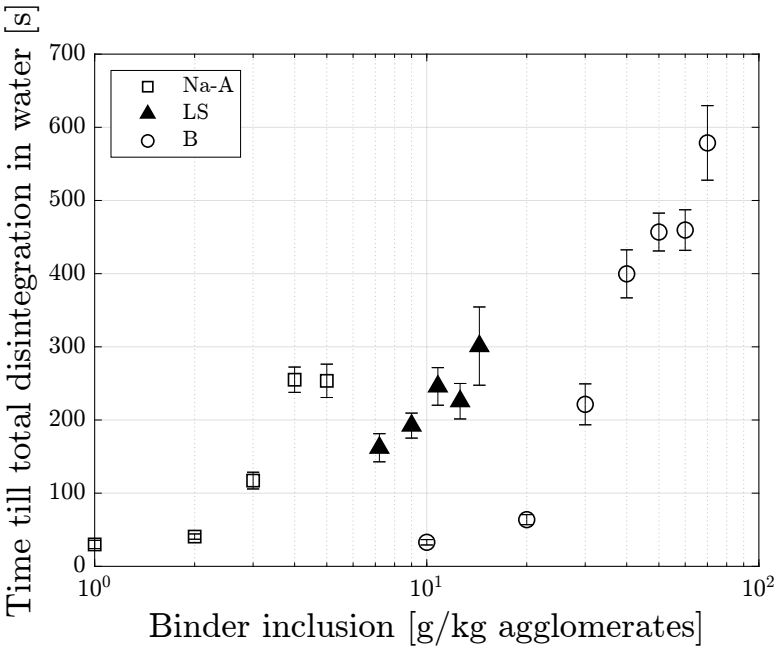
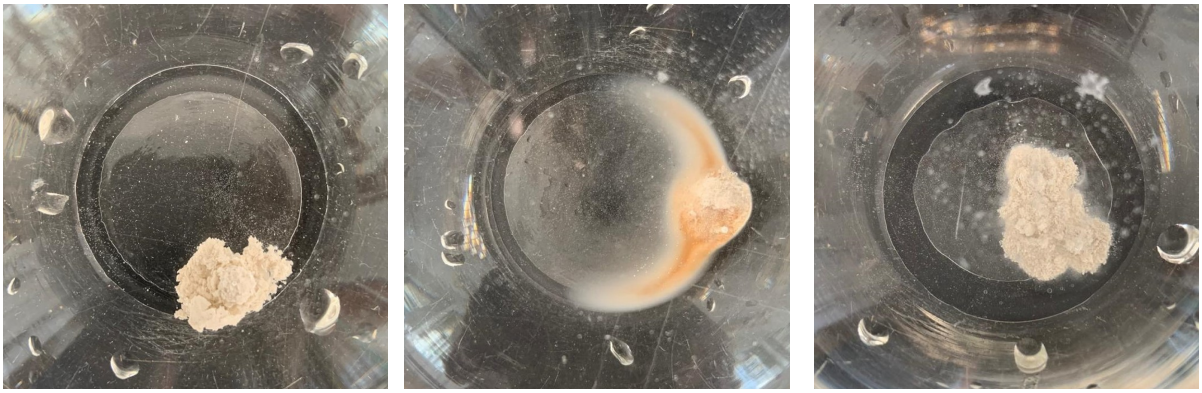


Figure 5.9: The average time it takes for agglomerates of different binder types, and concentrations thereof, to disintegrate when placed in 120 mℓ water. Symbols: □, sodium alginate; ▲, lignosulphonate; and ∘, bentonite

As the test was carried out, it was evident that the different binders experienced different modes of disintegration. Figure 5.10 shows the disintegrated remains of the agglomerates at the end of the moisture disintegration test. Sodium alginate exhibited flake-like disintegration, where small sheets separated from the nucleus of the agglomerate, until its shape was completely lost. This mode of disintegration was owed to the ionic cross-linking of the sodium alginate polymers and the calcium ions in the limestone and the strong inter-particle bonds that created. The lignosulphonate-limestone agglomerates relied on the solubility of the sulpho-groups in the lignosulphonate for disintegration. As these agglomerates were placed in the water, a brown region surrounded the agglomerates where the lignosulphonate had solubilised in the water. Over time, the agglomerate lost shape with the removal of the binder to the surrounding water. The swelling capability of the bentonite agglomerates



(a) Flake-like (Sodium Alginate) (b) Heaped remains (Lignosulphonate) (c) Burst open remains (Bentonite)

Figure 5.10: The different modes of disintegration followed by the three different binder types in a limestone agglomerate.

aided in the durability of the agglomerates, as well as the means in which it disintegrated. When the bentonite-limestone agglomerates were placed in the water, the bentonite absorbed the water, allowing the agglomerate to swell. This continued until the agglomerate was too large for internal adhesive forces, causing it to *burst* open. As the agglomerate *burst* open, it covered a larger surface area at the base of the beaker than before. This suggested that when saturated on the soil surface, the bentonite-limestone agglomerates would *burst* and cover an increased surface area on the top soil. The increase in concentration of bentonite in an agglomerate allowed for the agglomerate to absorb a larger volume of water before *bursting* open; leading to an the increase in time that it could remain intact when placed in water.

Sodium alginate contributed approximately 66 seconds per gram of binder included per kilogram agglomerate, whereas lignosulphonate and bentonite contributed $\approx$ 17 and $\approx$ 9 seconds per gram of binder, respectively. Therefore, although sodium alginate disintegrated faster than the other two binders, the binder played more of a role in resisting disintegration than the other two. Agglomerates with concentrations of 4 g and 5 g sodium alginate per kilogram, performed competitively with those of the 10.8-14.4 g lignosulphonate- and 30 g bentonite-agglomerates, whereas those of 40-70 g bentonite per kilogram resisted disintegration longer than that of the other agglomerate types. The swelling properties of bentonite support this result, as the agglomerates of increased bentonite inclusion had the capacity to swell more prior to disintegration.

The agglomerates that resisted disintegration for the longest period of time indicated that their disintegration would take place over time, rather than after the first rain or period of irrigation, or worse, when exposed to moisture in transportation or handling. As there is a lack of literature for uncoated agglomerates of this size, the absolute criteria for moisture disintegration should be determined *in situ*. Regardless, this test offered insight into the relative resistance to moisture degradation of the agglomerates and a comparison could be drawn when considering the average results of the agglomerates tested. With this, the average resistance time that the agglomerates remained intact for, was 237 seconds, and those agglomerates that resisted disintegration for longer than the average were considered preferable over those that did not.

5.4.5 Total strength and desirability

The total strength of a limestone agglomerate with a certain binder concentration was dependent on the impact strength, abrasive strength, compressive strength and resistance to moisture degradation. Table 5.1 shows how each of the different agglomerate types fared with regards to each of the different strength tests. The table confirms that there was a positive relationship between the concentration of a specific binder and the number of tests that the agglomerate type satisfied, hinting at the strength of the product.

An agglomerate of higher strength was preferred as it will be able to resist degradation during the processes prior to application to the soil. Therefore, an agglomerate that performed well in the tests was considered preferable over an agglomerate that did not, which follows the notion that if the agglomerate could not satisfy most of the tests, it would not be strong enough for use on a commercial scale. The agglomerates of 10.8-14.4 g lignosulphonate or 30-60 g bentonite per kilogram performed well in some tests, but would not be strong enough to withstand compressive stresses associated with the process prior to application, such as when packed in stockpiles during transportation or storage. These agglomerates also performed poorly in terms of impact strength in comparison with those of 3-5 g sodium alginate- and 70 g bentonite per kilogram and should therefore not be considered for industrial use.

Calcium ions generally bond weakly with lignosulphonate (Grierson, Knight, and Maharaj, 2005), supporting the poor strength of the lignosulphonate-limestone agglomerates at the concentrations tested. The agglomerates of 4-5 g sodium alginate and 70 g bentonite per kilogram proved to be of industrial interest in terms of strength, as they performed well in all the tests. Although the agglomer-

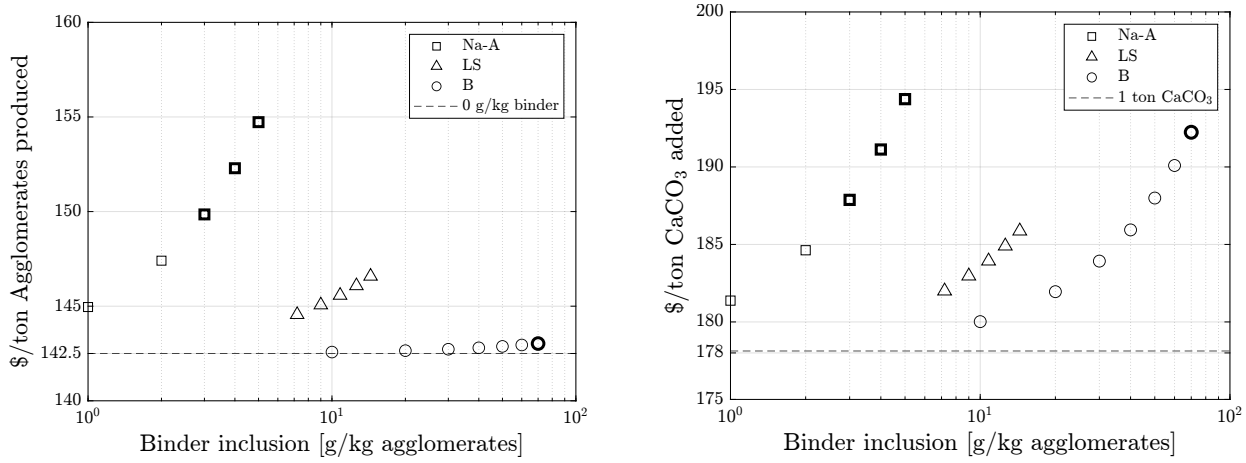
Table 5.1: An indication of whether (+) or not (-) the binder types - sodium alginate (Na-A), lignosulphonate (LS) and bentonite (B) - at various concentrations satisfy the chosen criteria for each strength test.

Binder g/kg	Drop - < 7 ≤ +	Friability - > 5% ≥ +	Compression - < 14 N ≤ +	Disintegration - < 237s ≤ +	Tests satisfied
Na-A 1	-	-	-	-	0
Na-A 2	-	-	-	-	0
Na-A 3	+	+	+	-	**3**
Na-A 4	+	+	+	+	**4**
Na-A 5	+	+	+	+	**4**
LS 7.2	-	-	-	-	0
LS 9.0	-	+	-	-	1
LS 10.8	-	+	-	+	2
LS 12.6	-	+	-	+	2
LS 14.4	-	+	-	+	2
B 10	-	-	-	-	0
B 20	-	-	-	-	0
B 30	-	-	-	-	0
B 40	-	+	-	+	2
B 50	-	+	-	+	2
B 60	-	+	-	+	2
B 70	+	+	+	+	**4**

ates of 3 g sodium alginate per kilogram did not perform as well in the moisture degradation test, they were still considered to be of industrial interest as they performed well in terms of impact, abrasive and compressive strength, which was satisfactory if the agglomerates were protected from significant levels of moisture in the processes prior to its application to the soil.

For an agglomerate to be considered worthwhile on a commercial scale, it should be durable enough to withstand the stresses that it may experience prior to application, while also maintaining affordability. While the strength of the agglomerates were compared to one another, the cost of the binder should be justified by the strength that it provides. A consumer will be attracted to a product of low cost and high strength, as a product of too low a strength will likely break prior to application and would therefore not be acceptable, regardless of the cost. The cost of the binder and the concentration thereof has an impact on the cost of the final agglomerated product, where Figure 5.11a shows the cost to produce a ton of each agglomerate type.

Commercial farmers may be interested in the cost of the value product ($CaCO_3$) that is applied to the soil, as calculations are carried out on commercial farms to determine the amount of $CaCO_3$/ha required to increase the soil pH to an acceptable value (limes requirement tests). Therefore, Figure 5.11b shows the cost per ton of the value product, $CaCO_3$, that can applied to the soil. The results consider that the limestone was not pure $CaCO_3$, but rather a high percentage thereof, where this was calculated as 80% for the limestone used. This cost calculation also accounted for the different concentrations of limestone powder included for each of the agglomerate types as a result of the supplementary binder inclusion. The results marked in bold in Figures 5.11a and 5.11b are those that performed acceptably in the strength tests and were considered to be of industrial interest from the results in Table 5.1. *Pro-pelleted* calcitic limestone is a pelleted limestone that can be bought on a commercial scale for $350.00 per ton of product. This limestone product is similar to the limestone agglomerates that were produced in this thesis, with 80% $CaCO_3$ and 8% $MgCO_3$ (Oldcastle stone products, 2018).



(a) The cost per ton of agglomerates added to the soil.

(b) The cost per ton of $CaCO_3$ added to the soil.

Figure 5.11: The cost ($) per ton of agglomerates and limestone powder added to the soil with the use of different binders.

Figure 5.11a shows that 1 ton of industrial grade limestone was approximately $142.50, where adding different binders increased the price, but also improved the physical characteristics of the product. It was approximately 4-8% more expensive to produce a ton of strong sodium alginate agglomerates

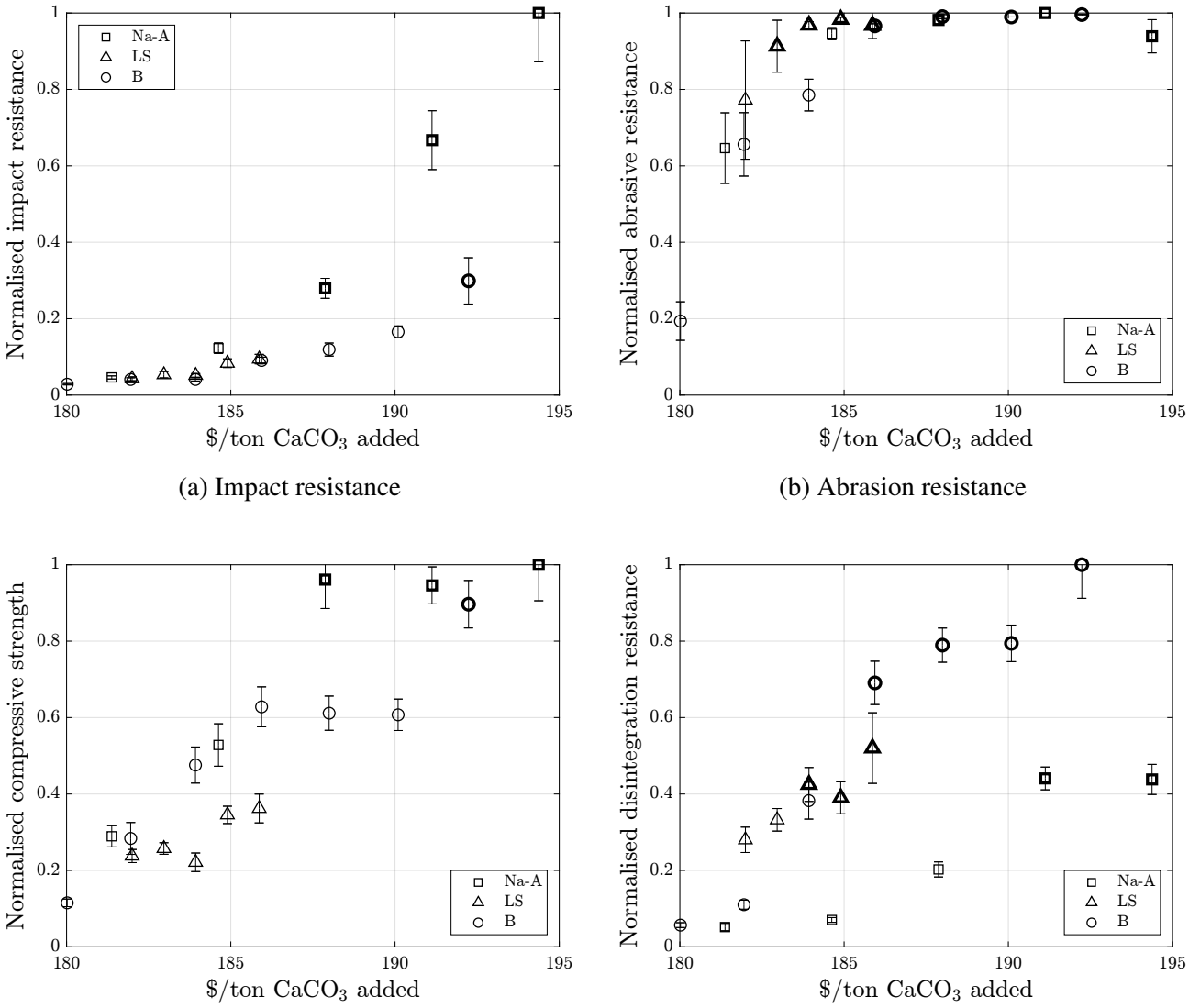
compared to that of strong bentonite agglomerates. It is however important to consider that the bentonite agglomerates have a lower concentration of $CaCO_3$ due to the higher concentration of binder.

The cost calculation used for Figure 5.11b considered that only 80% of the limestone powder used was $CaCO_3$, where the amount of limestone powder equivalent to 1 ton of pure $CaCO_3$ costs approximately \$178. The results show that the cost of the $CaCO_3$ was relatively similar for stronger agglomerates of 3-5 g sodium alginate and 70 g bentonite per kilogram. Limestone powder was included in relatively high percentages ($< 90\%$) in all of the agglomerates, therefore the cost of the value product was highly dependent on the cost of the limestone, explaining why the different binders follow a similar trend in Figure 5.11b.

The benefit of the low concentration of sodium alginate was offset by its higher price, making lignosulphonate and bentonite competitive with it even if included at higher concentrations. Agglomerates of 3-5 g sodium alginate and 70 g bentonite per kilogram were the result of a 5-9% increase in the cost of the raw, unagglomerated limestone powder. The benefit of avoiding the loss of product due to the dispersion of limestone powder in windy conditions should outweigh the added cost of binder used to agglomerate the limestone. The additional strength that these stronger agglomerates exhibited would result in a larger proportion of whole, undamaged agglomerates that can be applied to the soil - which would be in the best interest of both the supplier and the user. This too may be true for lignosulphonate-limestone agglomerates of a higher binder concentration if the trends seen in the strength tests are followed.

Although Table 5.1 shows how the agglomerates fared with regards to the strength tests, it was beneficial to visualise how the added costs associated with adding the different binders influenced the performance of the agglomerate types in the different tests. Figure 5.12 shows how the normalised strength test results compare to the cost of $CaCO_3$ that can be applied to the soil. The normalised values allowed each of the agglomerate types to be compared to the best performing agglomerate type for that test.

The bold symbols in Figure 5.12 represent those agglomerates that satisfied the tests as per the criteria set out in Table 5.1. Figure 5.12a shows that the cost added with increased binder concentration proved beneficial in terms of the agglomerates' resistance to breaking due to impact stresses. The more expensive, sodium alginate binder proved to be worth the added cost, where sodium alginate agglomerates increased with ≈ 0.075 points ($R^2 = 0.9317$) on the normalised impact resistance scale for each \$1 spent on the agglomerates, through the addition of binder. This was 5.5 and 3.75 times the amount



(a) Impact resistance

(b) Abrasion resistance

(c) Compressive resistance

(d) Moisture disintegration resistance

Figure 5.12: The normalised results of each of the strength tests, with results compared to the cost of the value product, $CaCO_3$, that was added to the soil. Symbols: □ sodium alginate; Δ lignosulphonate; and ∘ bentonite. Bold symbols represent those that satisfy the test, shown in Table 5.1.

of improvement that resulted from a \$1 increase in cost of lignosulphonate-limestone (R^2 = 0.8828) and bentonite-limestone (R^2 = 0.8482) agglomerates, respectively. With that, even though the most expensive bentonite agglomerate tested (70 g bentonite/kg) was similar in price to the most expensive sodium alginate agglomerates tested (5 g sodium alginate/kg), it performed approximately a third as well in resisting breakage on impact.

Figure 5.12b paints a different picture, with the majority of the graph showing a horizontal relationship between the abrasive resistance and the cost, supporting the suggestion that after a certain amount of binder was added, the abrasion resistance remained relatively good irrespective of the binder used. Therefore, the added cost of the sodium alginate and high inclusions of bentonite did not seem to impact the agglomerates' resistance to abrasion. Although, the agglomerates that cost the least did perform poorly in this test, the agglomerates of more than \$183/t $CaCO_3$ performed similarly to those in the region of \$190/t $CaCO_3$. This was however only true for the abrasive resistance, where industrial viability of a cost saving would require that the agglomerates are strong in all aspects.

Figure 5.12c shows that sodium alginate- and bentonite-limestone agglomerates were of similar value in terms of the compressive strength associated with the cost of the products. An additional \$1 of value added to sodium alginate- (R^2 = 0.8316) and bentonite-limestone (R^2 = 0.8885) agglomerates proved to add approximately 0.05 points on the normalised compressive strength scale each. Lignosulphonate-limestone agglomerates only contributed 0.035 (R^2 = 0.6816) additional compressive strength points for each \$1 added to the material costs of the product. Sodium alginate and bentonite were therefore more than 55% more cost effective than lignosulphonate in producing a product of high compressive strength. The horizontal relationship between the sodium alginate agglomerates at \$188-\$194/t $CaCO_3$ suggests that sodium alginate-limestone agglomerates of \$188/t $CaCO_3$ can be competitive with the sodium alginate agglomerates of increased binder concentration and therefore material costs. This is a cost saving of approximately 3% for similar compressive strengths in sodium alginate agglomerates.

Figure 5.12d suggests that bentonite was most cost effective in reducing the rate at which an agglomerate disintegrates. Bentonite-limestone agglomerates resisted degradation in water for approximately 45% longer than lignosulphonate (R^2 = 0.8617) for each \$1 cost added to the agglomerates. With bentonite improving by 0.08/\$ (R^2 = 0.9373) on the normalised scale, it was 129% more cost effective than sodium alginate (R^2 = 0.9001) in resisting disintegration when exposed to moisture.

If there was a high probability that the agglomerates would be exposed to significant amounts of mois-

ture in the processes prior to application, it may be worthwhile in investing in the agglomerates of high concentration of bentonite, or do further testing of sodium alginate- or lignosulphonate-limestone agglomerates at higher concentrations than what was tested. If the agglomerates are likely to remain dry throughout the processes prior to application, this strength index may be less important than the mechanical strength tests in Figures 5.12a, 5.12b and 5.12c. If a dry environment were to be considered and the moisture disintegration results were deemed less significant, producing a sodium alginate agglomerate at \$188/t would be in the region of 1.6-3.5% cheaper than a more expensive sodium alginate- or bentonite-limestone agglomerate type, while being of similar mechanical strength. If moisture resistance were significant, the bentonite agglomerate of \$192/t $CaCO_3$ would be a viable option as it performed well in all the tests, including the moisture disintegration test. In order to have the lignosulphonate-limestone agglomerates perform similarly in terms of strength to this \$192 bentonite-limestone agglomerate it would have to have an increase in binder concentration, resulting in an approximate material cost of \$201.50/t $CaCO_3$ - $\approx$ 5% more expensive. The resulting agglomerate of 43 g lignosulphonate per kilogram would perform less than 3% better in terms of mechanical strengths and resist disintegration in moisture approximately 30% better. The only slight increase in mechanical strength is therefore not worth the additional cost, as bentonite-limestone agglomerates of \$192/t $CaCO_3$ resists moisture degradation sufficiently already.

Sodium alginate has proven to be a mechanically strong binder for limestone agglomerates. However, to have an agglomerate of sodium alginate resist moisture degradation competitively with the \$192/t $CaCO_3$ bentonite-limestone agglomerates, the product would require an increase in binder resulting in a material cost of approximately \$209/t $CaCO_3$. Although almost 9% more expensive with a concentration of 9 g sodium alginate per kilogram agglomerates, this is predicted to produce a product that is $\approx$ 96% and 105% stronger than the \$192/t $CaCO_3$ bentonite agglomerates in impact- and compressive resistance, respectively.

The agglomerates with concentrations of 4-5 g sodium alginate and 70 g bentonite per kilogram did however appear to resist wear sufficiently when exposed to the stresses involved in the processes prior to application. They were also competitive in price with each other, as well as with the \$350.00/t *Pro-Pelleted* calcitic limestone available on the market. Sodium alginate and bentonite included at these concentrations are therefore prospective alternatives as binders in the agglomeration of limestone.

5.5 Soil lime requirement

The agglomerates of a binder concentration that were determined to be of the strongest for the specific binder type, were to be applied to artificial soil columns to treat any soil acidity. However, in order to determine the amount of limestone that should be applied to the soil to increase the pH to an appropriate range, a limestone requirement test was carried out. The soil that was used for this research was obtained in Caledon, South Africa, with the Eksteen lime requirement test (Eksteen, 1969) an appropriate choice for South African soil.

After preparation of the < 2 mm air-dried soil, discussed in Section 4.5, the soil underwent ICP analysis in order to obtain the amount of available Ca^{2+} and Mg^{2+} available. This test was repeated in triplicate with an average result of 0.419 cmol.kg^{-1} Ca^{2+} and 0.525 cmol.kg^{-1} Mg^{2+}, in the soil sample. The total calcium and magnesium ($Ca + Mg$) of 0.944 cmol.kg^{-1} was therefore calculated as the sum of these two results. The titratable acidity of the < 2 mm soil sample was obtained using the titration method described in Section 4.5. It was determined that the average volume of NaOH required in order to obtain the permanent pink endpoint of the titration, was 3.3 mℓ. Using Equation 4.8 the titratable acidity (H) was determined as 0.33 cmol.kg^{-1}.

With the use of Equation 4.10 and using an R-value of 10, the limestone requirement of the soil was calculated to be 1.114 t/ha $CaCO_3$. This result is in the range of 1-1.5 t/ha that was recommended by Dr Pieter Swanepoel (Stellenbosch University) for liming of soil of this type, from the region investigated.

The limestone requirement was used to determine how much of the agglomerates were needed in the amelioration of soil acidity in the soil columns discussed in Section 4.6.

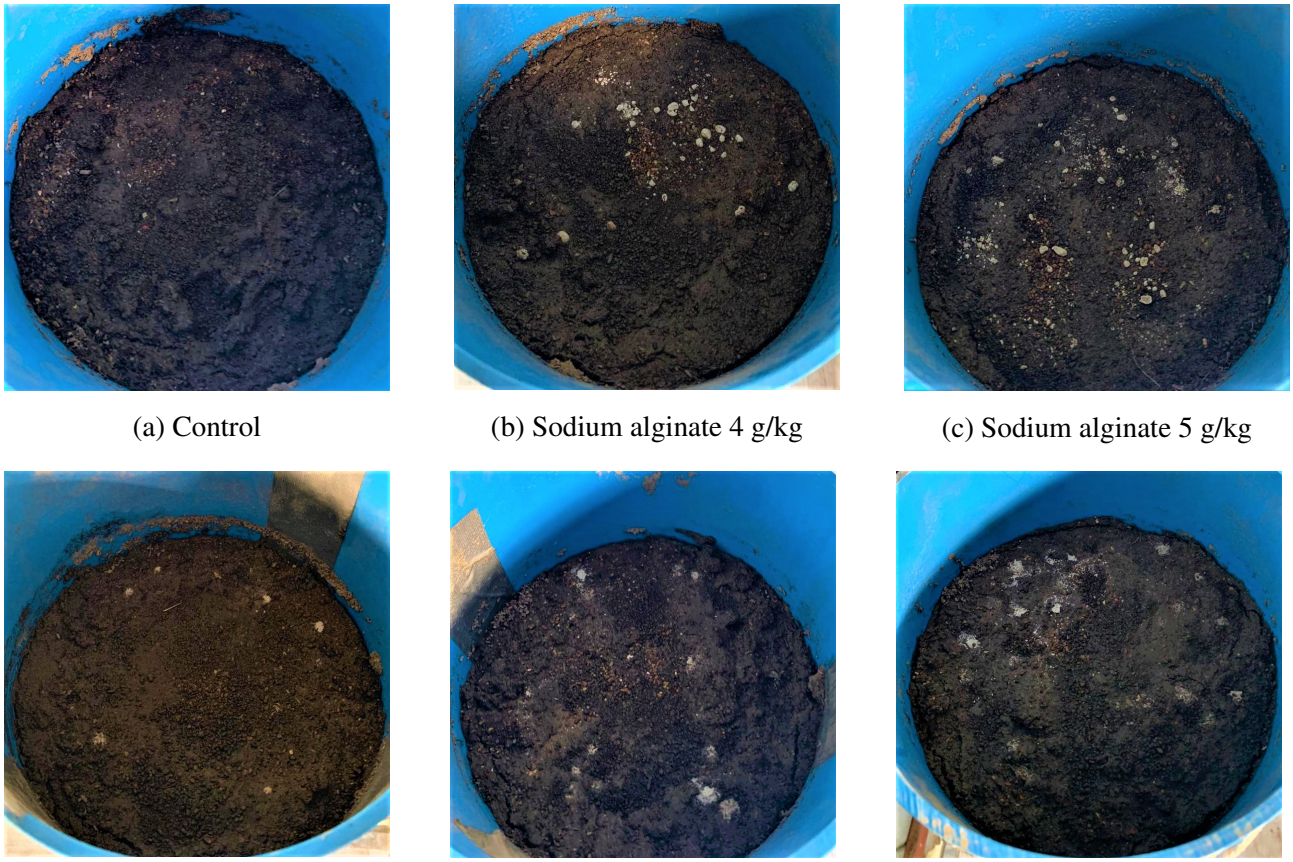
5.6 Effect of the pellets on a soil profile

Six soil columns were packed using soil from Skilpadsgat Farm, Caledon. The mass of agglomerates placed on each of the soil columns was calculated with the binder and limestone concentration, as well as $CaCO_3$ content considered. The agglomerates that were used in this section had binder concentrations of:

- 4 g and 5 g sodium alginate,

- 14.4 g lignosulphonate, and
- 40 g and 70 g bentonite per kilogram agglomerates.

The agglomerates of each agglomerate type were placed on the surface of the soil columns, whereafter the columns were exposed to a 3 month rain simulation for May-July 2015 in Malmesbury, South Africa. This year was selected as it had the closest total rainfall of 174.4 mm when compared to the average rainfall for that period over 2014-2017 of 178.3 mm.



(a) Control (b) Sodium alginate 4 g/kg (c) Sodium alginate 5 g/kg

(d) Lignosulphonate 14.4 g/kg (e) Bentonite 40 g/kg (f) Bentonite 70 g/kg

Figure 5.13: The surface of the soil columns, showing how the agglomerates had disintegrated after a 14 week rainfall simulation.

The limestone agglomerates would ideally have broken down under irrigation of the column and either

slightly dissolved in the surface water or the fine lime particles would have been transported along with the water as it filtered through the soil column. The figures in Figure 5.13 show the surface of the columns after the rain simulation, where the white specks show limestone that remained on the surface. It is clear in Figure 5.13b and 5.13c that the sodium alginate agglomerates did not fully break up during the rain simulation. This could be due to the flake-like disintegration that was seen in the moisture disintegration test and Figure 5.10a. Larger particles of sodium alginate-limestone that remained atop the surface of the soil column, were too large to penetrate the top layer of soil.

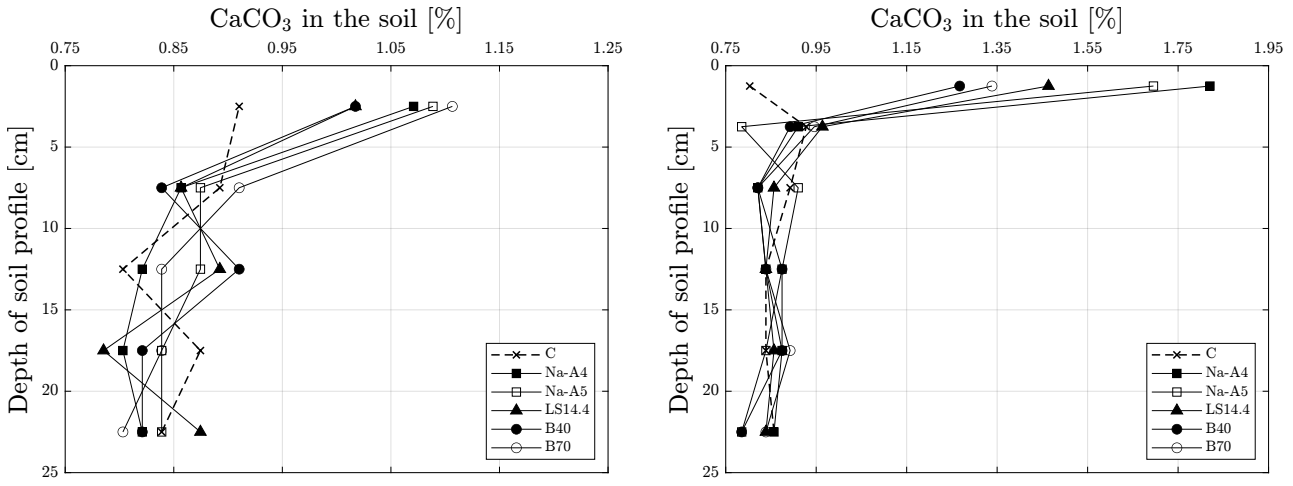
In the moisture disintegration test, Figure 5.10b shows how the lignosulphonate-limestone agglomerates disintegrated into fine particles that spread into the surrounding water, allowing the limestone to either dissolve into the water or move deeper into the soil column with it. The lignosulphonate agglomerates appear to have disintegrated nearly fully in Figure 5.13d, where far less white limestone remained on the soil surface. This is supported by the water soluble nature of the lignosulphonate binder, allowing the agglomerates to easily break up into fine particles of limestone, fine enough to penetrate the first layer of soil particles.

Although the agglomerates of 70 g bentonite per kilogram proved to take the longest to disintegrate in Figure 5.9 (Section 5.4.4), they appeared to have disintegrated nearly fully in Figure 5.13f, suggesting that a 3 month winter rainfall period is sufficient for the agglomerates to disintegrate. The bentonite agglomerates of 40 g and 70 g per kilogram, both appear to have disintegrated and remain spread atop the surfaces of the soil columns in Figure 5.13e and 5.13f, respectively. Once again, the scattered appearance of the disintegrated agglomerates is supported by the mechanism of disintegration observed in the moisture disintegration test and Figure 5.10c. The bentonite-limestone agglomerates appeared to *burst* when saturated with water, increasing the surface area of the limestone that was exposed to the top layer of soil. The broken up bentonite-limestone agglomerates appeared to be in the form of the fine limestone, rather than *flakes* as was the case with sodium alginate. Less limestone on the surface of the bentonite soil columns, compared to that of the sodium alginate columns supported this - the bentonite-limestone agglomerates disintegrated to micro-fine powder that could have either dissolved into the water or penetrated the top layer of the soil particles, similarly to the lignosulphonate-limestone agglomerates.

Although the surface of most of the soil columns showed that some of the agglomerates remained atop the soil surface, others showed that the agglomerates had broken up allowing the limestone to potentially filter through the soil column. Further testing was required to show this. The soil columns

were therefore segmented at 5, 10, 15, 20 and 25 cm deep for the first time the column experiment was run. With the second soil column experiment, the columns were segmented at 2.5, 5, 10, 15, 20 and 25 cm in order to discuss the top soil in more detail.

An XRF analysis was carried out on a sample from each of the soil segments, where the CaO result was used to give an indication of the amount of $CaCO_3$ present in sample (XRF results are shown in Appendix I). This was possible through the assumption that CaO was bonded to CO_2 as $CaCO_3$. Figure 5.14a shows the results for the first soil column experiment, where Figure 5.14b shows the results of the repeat or second soil column experiment.



(a) Repeat 1

(b) Repeat 2

Figure 5.14: The amount of $CaCO_3$ measured at different depths of the soil column after the soil was exposed to limestone agglomerate application and 3 months of simulated rainfall. Symbols: × control; □ sodium alginate 5 g/kg; ■ sodium alginate 4 g/kg; ▲ lignosulphonate 14.4 g/kg; ● bentonite 40 g/kg; ∘ bentonite 70 g/kg.

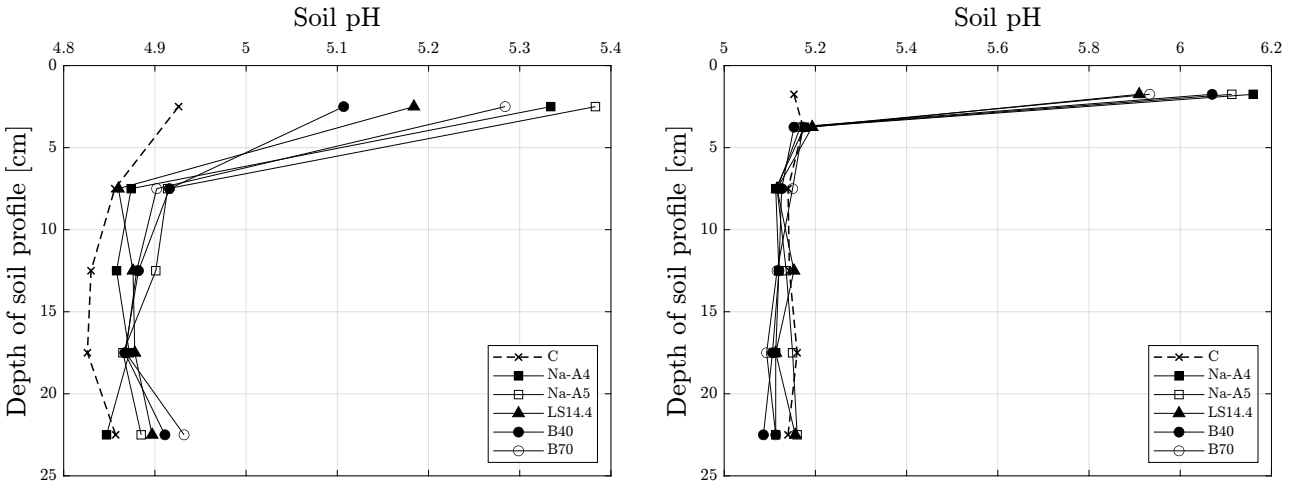
Figure 5.14 shows the clear relationship between the soil columns that had limestone agglomerates placed on them and the increase in $CaCO_3$ on the soil surface. The control had no limestone applied to it and although there were fluctuations in the amount of $CaCO_3$ recorded, the amount of $CaCO_3$ in the soil at different depths remained relatively constant. Figures 5.14a and 5.14b show that the amount of $CaCO_3$ in the soil was similar to that of the control at depths below the reading closest to the surface. This suggests that the limestone did not successfully move through the soil profile to

depths lower than 2.5 cm from the surface.

The individual results were also supported by results shown in the strength tests in Section 5.4, mostly related to the modes of disintegration during the moisture disintegration tests. The sodium alginate agglomerates appear to have the most $CaCO_3$ in the top soil of columns, supported by the notion that the flake-like moisture disintegration that occurred in Figure 5.10a further prevented the limestone from penetrating through the slightly packed soil to deeper levels. During homogenising of the soil, the flakes may also not have disintegrated to fines, due to their strong bonds, placing more $CaCO_3$ in the sample that was sent for XRF analysis, over the finer disintegrated agglomerates of lignosulphonate and bentonite. The smaller change in $CaCO_3$ between the 0-5 cm and the deeper segments, and the 0-2.5 cm segment and deeper segments in Figure 5.14a and 5.14b respectively, was a result of the limestone likely staying in the 0-2.5 cm region of the soil profile, where it was mixed with unlimed soil of the 2.5-5 cm region. This would have diluted the reading of $CaCO_3$ in the top layer of soil in Figure 5.14a, where Figure 5.14b shows that the limestone did not filter to any significant depth of the soil column.

The soil was also tested for changes in pH and electrical conductivity along the soil profile due to the addition of the limestone agglomerates. Figure 5.15a and 5.16a show the pH and EC readings from the first experimental run with segments of 5, 10, 15, 20 and 25 cm deep into the soil profile. Figure 5.15b and 5.16b show the pH and EC readings obtained from the second soil column experimental run with more detail near the surface, with additional data from segment samples at 0-2.5 cm and 2.5-5 cm of the soil profile.

Although Figures 5.15a and 5.15b are results from 2 different soil column experiments, the results were similar. The link between limestone added to soil and the increase in pH was supported by the amount of $CaCO_3$ found in the soil through XRF, in Figure 5.14. With the lack of movement of the $CaCO_3$ through the soil profile, the pH did not change significantly at levels deeper than the top layer of the soil columns. The more variable average pH recording in the 0-5 cm segment of Figure 5.15a may be owed to the suggestion made in Figure 5.15b that the soil that contributed to the recorded increase in pH was in the top 0-2.5 cm segment, where the difference in soil pH was then diluted when it was mixed with the bottom 2.5-5 cm in a 0-5 cm soil segment. The large difference in pH between the top- and bottom-segments in Figure 5.15b compared to that of Figure 5.15a was also owed to the high concentration of $CaCO_3$ in the top 0-2.5 cm that changed the pH, whereas in Figure 5.15a this was mixed with soil (2.5-5 cm) of a lower pH.



(a) Repeat 1

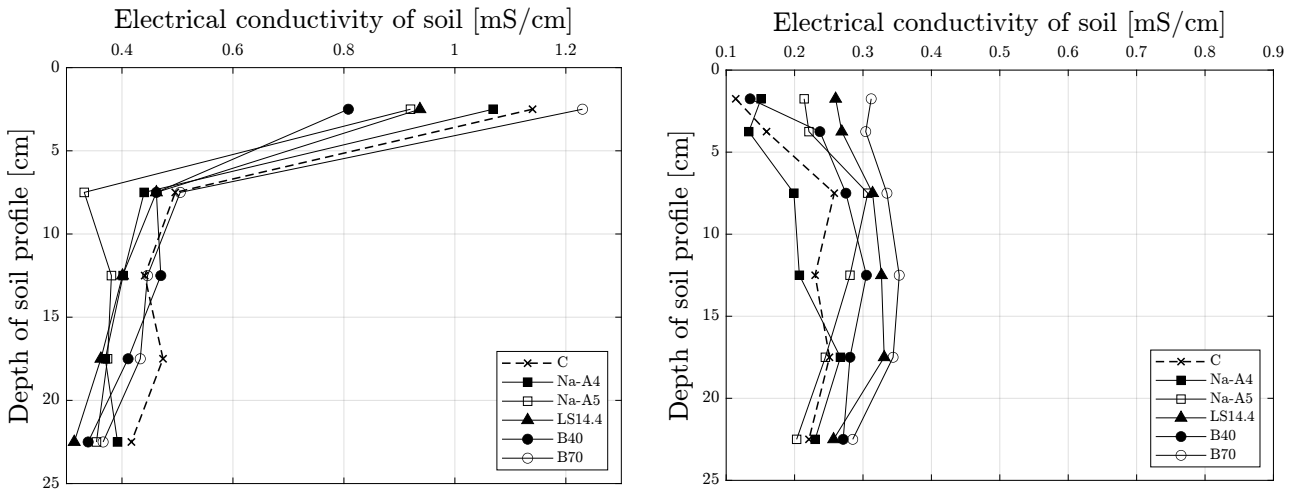
(b) Repeat 2

Figure 5.15: The pH readings taken from the different depths of the soil column after the soil was exposed to limestone agglomerate application and 3 months of simulated rainfall. Symbols: × control; □ sodium alginate 5 g/kg; ■ sodium alginate 4 g/kg; ▲ lignosulphonate 14.4 g/kg; ● bentonite 40 g/kg; ∘ bentonite 70 g/kg.

The relatively insoluble property of $CaCO_3$ is also a major role player in the lack of pH change lower down the soil profile. Although the water applied to the soil column did filter through the soil profile, it is evident that the limestone did not sufficiently dissolve into the water to increase the pH of the soil.

The electrical conductivity of samples taken from each of the soil segments was also tested. Figure 5.16a shows the EC measured in the first soil column experiment, whereas 5.16b shows the EC measured on the 6 samples from each of the columns in the second soil column experiment.

Figure 5.16a shows an increase in electrical conductivity in the first 0-5 cm of the soil profile, whereas the electrical conductivity remained relatively constant in the lower 5-25 cm. Figure 5.16b shows a different result in the repeat of the experiment, where the electrical conductivity of the different segments remained relatively similar throughout the vertical of the soil profile. Although the different runs of the same experiment give different results, similar conclusions could be drawn. The results in both figures show that the limestone-treated columns followed the same trends to that of the unlimed control. This consistent result is supported by the insoluble nature of limestone, suggesting that it did not significantly alter the ionic activity of the soil. Electrical conductivity is generally used as a



(a) Repeat 1

(b) Repeat 2

Figure 5.16: The electrical conductivity readings taken from the different depths of the soil column after the soil was exposed to limestone agglomerate application and 3 months of simulated rainfall. Symbols: × control; □ sodium alginate 5 g/kg; ■ sodium alginate 4 g/kg; ▲ lignosulphonate 14.4 g/kg; ● bentonite 40 g/kg; ∘ bentonite 70 g/kg.

measure of salts in the soil, related to the amount of nitrates, sodium, potassium, chlorides, sulphates and ammonium in the soil. Ions may have been leached from the soil during the application of the water, where this also occurred in the control and can therefore not be regarded a consequence of limestone application.

The results shown in Figures 5.14 and 5.15 therefore suggest that there was no significant movement of the limestone through the soil profile and that the agglomerates did not impact the soil pH at levels lower than the surface. The electrical conductivity of the soil was not significantly impacted by the application of limestone, due to its relative insolubility. This conclusion was supported by literature, where Li et al. (2019) and Blevins, Murdock, and Thomas (1978) found that it took multiple years for limestone to move through a soil profile and/or ameliorate soil acidity at any depths lower than 5 cm from the surface.

5.7 Summary

An inclined disc agglomerator was designed and manufactured for the production of limestone agglomerates. The agglomeration procedure was investigated using 2^2 CCDs, with reference to the speed of rotation, volume of liquid added to the system and binder concentration included in the product. Speed of rotation and binder concentration were found to have an insignificant impact on the mass fraction of agglomerates produced in the +2 -5.6 mm diameter range. The volume of liquid added to the system was however found to have a significant impact on this yield, where sodium alginate, lignosulphonate and bentonite required 20 mℓ, 18 mℓ and 22 mℓ of liquid to maximise this yield for 100 g of dry powder. Agglomerates produced with these volumes of liquid and different binder concentrations for each of the binder types, underwent strength testing.

The agglomerates should be able to withstand the typical impact, abrasive, compressive and moisture stresses involved in the production, packaging, transportation and handling phases prior to application. Lignosulphonate at concentrations of 7.2-14.4 g/kg agglomerates could not satisfy the strength criteria set out for each of the aspects tested. However, sodium alginate at 4 g/kg and 5 g/kg and bentonite at 70 g/kg agglomerates were strong enough to satisfy the criteria set out in each of the strength tests and could be considered for industrial use. Lignosulphonate at 43 g/kg agglomerate would have theoretically been competitive with these agglomerate types if the trends for each of the tests were followed at higher binder concentrations, but this would have to undergo additional testing.

Agglomerates of each binder type were also placed on the surface of individual soil columns, and underwent a 14-week rain simulation. After XRF analysis, and pH and EC testing, it was found that although the agglomerates disintegrated on the surface of the soil columns, there was little to no movement of the limestone through the soil columns at depths deeper than 2.5 cm. As disintegration of the agglomerates did take place, it is however likely that given more time, the limestone would move through the soil columns to ameliorate soil acidity at levels deeper than the surface.

Chapter 6

Conclusions and recommendations

The aim of this project was to manufacture an inclined disc agglomerator that could be used to produce agglomerates of micro-fine limestone for the amelioration of soil acidity. The agglomerates had to have been in the size range that could be spread onto the soil surface using conventional agricultural spreading equipment. In order to ensure that the agglomerates would be strong enough to withstand typical impact, abrasive and compressive forces, as well as resist unwanted moisture degradation during production, packaging, transportation or storage processes, binders were used. The impact that sodium alginate, lignosulphonate and bentonite, and different concentrations thereof, had on these aspects of strength was to be investigated. Thereafter, the agglomerates were to be assessed to determine if with the application of rain or irrigation water, they would have had an impact on the pH of the soil at different depths of the soil profile, including at the surface.

A lab-scale inclined disc agglomerator was designed, manufactured and set to an incline of 45°, as per recommendations made in literature. In order to maximise the mass fraction of agglomerates that were in the +2 -5.6 mm diameter range, 2 CCDs were used along with 2 surface response ANOVAs. A CCD assessing the influence of speed of rotation of the inclined disc and the volume of liquid that was added to the system, concluded that in the range tested (20-55 rpm), the speed of rotation was not significant on the yield and was set to 37.5 rpm. The amount of liquid that was added to the system was determined as significant, leading to the second CCD, relating to the influence of binder concentration and liquid addition on the yield. The concentration of binder included in the agglomeration procedure did not have a significant impact on the yield of the agglomerates in the correct size range, however once again, liquid addition did for each of the binder types. This result supported literature in that the moisture content of the agglomerates during their formation was the primary factor in determining the size of the product. Sodium alginate required 20 mℓ of binder solution for 100 g of dry constituents, whereas lignosulphonate and bentonite required 18 mℓ and 22 mℓ respectively. These volumes were slightly lower than volumes included in the formation

of limestone agglomerates done in a previous study, but using a finer limestone, the inter-particle forces may have assisted in their agglomeration. Agglomerates were produced in the inclined disc agglomerator using the parameters obtained to maximise the yield for each binder type, at various binder concentrations. The investigation into the agglomerator was considered acceptable as the statistical yield and the actual yields were relatively similar and produced enough product for the remainder of the research.

Those agglomerates in the correct size range for each binder type and concentration thereof were assessed with regards to strength. Sodium alginate was included at 1-5 g per kilogram agglomerates, whereas lignosulphonate and bentonite where included at 7.2-14.4 g and 10-70 g, respectively. Even at lower concentrations, it was determined that sodium alginate provided the agglomerates with significantly more resistance to breakage as a result of impact forces, in comparison to lignosulphonate and bentonite. The agglomerates resisted abrasive wear similarly for higher concentrations of each binder type, whereas only sodium alginate and bentonite proved to resist compressive forces acceptably at the concentrations tested. Lignosulphonate did not perform well in resisting compressive stresses, but appeared to perform acceptably in resisting moisture degradation, as did bentonite and higher concentrations of sodium alginate. The strong chemical bonds that formed between the limestone particles in the presence of sodium alginate used as a binder was the result of ionic cross-linking that occurred between the calcium in the limestone and the sodium alginate polymers. Lignosulphonate and bentonite relied on adsorption techniques for bonding, which were not as strong as the sodium alginate bonds. However, bentonite included at 70 g/kg agglomerates were competitive with 4-5 g of sodium alginate per kilogram agglomerates. Lignosulphonate was not competitive with these agglomerate types at the concentration tested, however it was determined that at 43 g lignosulphonate per kilogram agglomerate, the resulting agglomerates would be similar in strength to those sodium alginate and bentonite agglomerates.

It was therefore successfully shown that the binder concentration had a significant impact on the overall strength of the limestone agglomerates. Also, of the binders tested, sodium alginate included at 4-5 g and bentonite included at 70 g per kilogram agglomerates were deemed successful in resisting breakage when exposed to impact, abrasive and compressive forces, as well as moisture degradation.

In terms of cost, the agglomerates of 4-5 g sodium alginate ($191-194) and 70 g bentonite ($192) per kilogram were relatively similar, whereas lignosulphonate agglomerates of the highest concentration (14.4 g/kg) were nearly 4% cheaper ($186). These cheaper lignosulphonate agglomerates were

however proven not strong enough for industrial use. The agglomerates of 43 g lignosulphonate per kilogram, were predicted to be strong enough, but were approximately 5% more expensive ($201) than those of sodium alginate and bentonite. Limestone agglomerates that are available on the market are however available to purchase at approximately double the material costs of the 4-5 g/kg sodium alginate and 70 g/kg bentonite-agglomerates, making these economically competitive for commercial scale.

Agglomerates of each binder type were also investigated to determine how they disintegrated under the application of a simulated rainfall and if the limestone could increase the pH of the soil at levels and deeper than the surface. The soil that was used underwent the Eksteen lime requirement test that determined that 0.01114 g/cm^3 $CaCO_3$ was required to ameliorate any soil acidity. With this, agglomerates of 4 g and 5 g sodium alginate, 14.4 g lignosulphonate, and 40 g and 70 g bentonite, per kilogram agglomerates were placed on artificial soil columns in masses determined by the lime requirement. Although the agglomerates did disintegrate, after a 14-week rain simulation, none of the columns experienced movement of the limestone to any levels deeper than 2.5 cm from the soil surface. This was supported by a lack of change in pH at levels below the top 2.5 cm of the soil. This concluded that the micro-fine limestone required a significantly longer period than 14-weeks to move to deeper levels in the soil columns, similar to what had been experienced with powdered limestone in previous research studies.

Recommendations

It is likely that lignosulphonate would be competitive with sodium alginate and bentonite when included at a higher concentration. It is therefore recommended that lignosulphonate is assessed with a concentration in the range of 20-50 g lignosulphonate per kilogram agglomerates. These agglomerates should undergo the same impact, abrasive, compressive, and moisture degradation tests undertaken in this research to determine if lignosulphonate is competitive with sodium alginate and bentonite when included at these concentrations.

It is also recommended to apply micro-fine limestone in powdered form to a soil column during a replication of the soil column tests, to determine if micro-fine limestone alters the pH of the soil at levels lower than the surface when not applied in agglomerate-form. This should give an indication of whether or not micro-fine limestone powder will move through the soil profile when not applied in agglomerate from. It would also assist in determining if the agglomeration and binder addition

influenced the lack of vertical movement of the limestone. With that, to determine if movement of the limestone through the soil will take place, the soil column trial should continue over a period of 12-18 months.

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Appendix A: Detailed and decoded CCDs

Table A.1: The decoded central composite design experimental design for rotational speed and liquid addition for sodium alginate (Na-A) at 2.5% concentration.

Standard order	Speed of rotation [rpm]	mℓ of liquid added
5	20	20
2	25	30
3	50	10
8	37.5	34
10 (C)	37.5	20
1	25	10
9 (C)	37.5	20
7	37.5	6
6	55	20
11 (C)	37.5	20
4	50	30

Table A.2: The decoded central composite design experimental design for rotational speed and liquid addition for bentonite-lime at a 4:96 g concentration.

Standard order	Speed of rotation [rpm]	mℓ of liquid added
5	20	30
2	25	40
3	50	20
8	37.5	44
10 (C)	37.5	30
1	25	20
9 (C)	37.5	30
7	37.5	16
6	55	30
11 (C)	37.5	30
4	50	40

Table A.3: The decoded central composite design experimental design for binder concentration and liquid addition for the production of sodium alginate-limestone agglomerates.

Standard order	Binder concentration [%/mℓ]	mℓ of liquid added
5	1.1	20
2	1.5	30
3	3.5	10
8	2.5	34
10 (C)	2.5	20
1	1.5	10
9 (C)	2,5	20
7	2.5	6
6	3.9	20
11 (C)	2.5	20
4	3.5	30

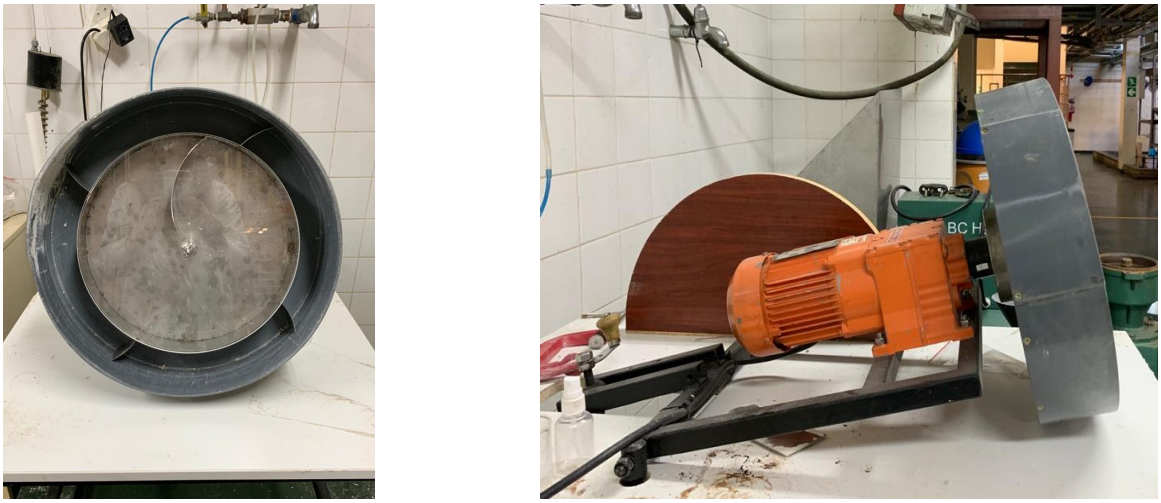
Table A.4: The decoded central composite design experimental design for binder concentration and liquid addition for the production of lignosulphonate-limestone agglomerates.

Standard order	Binder concentration [%/mℓ]	mℓ of liquid added
5	2	20
2	3	30
3	7	10
8	5	34
10 (C)	5	20
1	3	10
9 (C)	5	20
7	5	6
6	8	20
11 (C)	5	20
4	7	30
12	4	18
13	5	18
14	7	18
15	4	18
16	5	18
17	7	18

Table A.5: The decoded central composite design experimental design for binder concentration and liquid addition for the production of bentonite-limestone agglomerates.

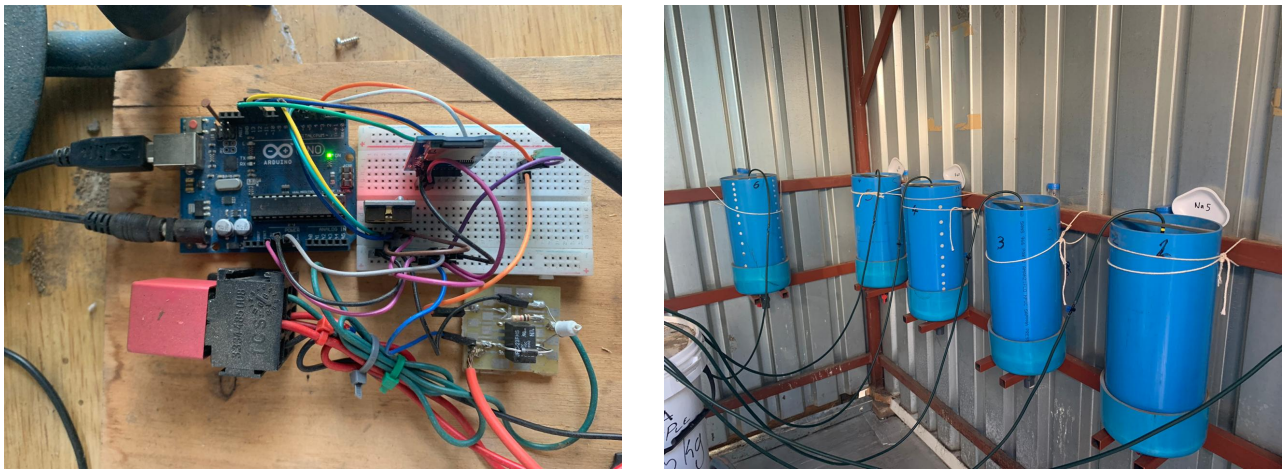
Standard order	Binder concentration [g/100 g]	mℓ of RO water added
5	1	30
2	2	40
3	4	20
8	3	44
10 (C)	3	30
1	2	20
9 (C)	3	30
7	3	16
6	5	30
11 (C)	3	30
4	4	40

Appendix B: Equipment used and experimental setup



(a) (b)

Figure B.1: The friability rig fitted to the disc agglomerator that was set to an incline of 10°.



(a) (b)

Figure B.2: The electronics (a) used to run the rain simulator that was used to automate the water applied to the soil columns (b)

Appendix C: Programmable code

Python code to extract maximum compression result

```
##Find Max Value in compression tests

import os
import re

filename = []
split = []
mo = []

def forceprint(filename, force):
    print(filename + " = " + str(force) + " N")
    return 0

path = """D:\\CompressionTests\\"""

for i in range (1,70):
    if i < 10:
        for r in range(5):
            filename.append("2020_0%s_0" % (i))
    else:
        for r in range(5):
            filename.append ("2020_%s_0" % (i))

for count in range (0,len(filename)):
        if len(filename[count]) == 9:
            if filename[count][6] == filename[count-1][6]:
                for j in range (1,5):
```

```
                    filename[count] = "%s%s.txt" % (filename[count], j)
                    count = count+1
            else:
                filename[count] = "%s0.txt" % (filename[count])

#print(filename)
LineRegex = re.compile(r'\d+.\d\d\d,\d.\d\d,\d+.\d\d')

for i in range (0,300):
    path2check = path + filename[i]
    if os.path.isfile(path2check):
        text = open(path2check, "r").read()
        mo = LineRegex.findall(text)
        #mo[0:5000]=[]
        for j in range(len(mo)):
            split.append((mo[j].split(",",2)[2]))
            split = list(map(float,split))
            force = max(split)
        split[0:len(mo)] = []
        forceprint(filename[i], force)
```

Matlab code for costing

```
set(groot,'defaulttextinterpreter','latex')
set(groot, 'defaultLegendInterpreter','latex');
set(groot, 'defaultAxesTickLabelInterpreter','latex')
set(groot,{'DefaultAxesXColor','DefaultAxesYColor','DefaultAxesZColor'},
{'k','k','k'})
t = 16;

%Cost

LA_cost = 2600/10^6;        %$/g Alibaba Group Organisation (2020a)
LS_cost = 430/10^6;         %$/g Alibaba Group Organisation (2020b)
B_cost = 150/10^6;          %$/g Alibaba Group Organisation (2020c)
CaCO3_cost =142.5/10^6;     %$/g Alibaba Group Organisation (2020d)

LA_l = [1 1 1 1 1]*10^6                    %g lime/ton pellets
LS_l = [1 1 1 1 1]*10^6
B_l = [0.99 0.98 0.97 0.96 0.95 0.94 0.93]*10^6

LA_b = [0.1 0.2 0.3 0.4 0.5].*10^4;        %g binder/1000kg pellets
LS_b = [0.72 0.9 1.08 1.26 1.44].*10^4;
B_b = [1 2 3 4 5 6 7].*10^4;

LA_tw = LA_l + LA_b;                % total weight
LA_pt = 10^6./LA_tw;                % per ton pellets
LA_CCE = (10^6./(0.8*LA_l))         % ton pellets per ton CaCO3

LS_tw = LS_l + LS_b;
LS_pt = 10^6./LS_tw;
LS_CCE = (10^6./(0.8*LS_l))

B_tw = B_l + B_b;
```

```
B_pt = 10^6./B_tw;
B_CCE = (10^6./(0.8*B_l))

LAb_cost = (LA_b*LA_cost + LA_l*CaCO3_cost).*LA_pt;   %Sale cost
LAb_cost1 = (LA_b*LA_cost + LA_l*CaCO3_cost).*LA_CCE; %CaCO3 added price
LAc = (LAb_cost./SLA)

LSb_cost = (LS_b*LS_cost + LS_l*CaCO3_cost).*LS_pt;   %Sale cost
LSb_cost1 = (LS_b*LS_cost + LS_l*CaCO3_cost).*LS_CCE; %CaCO3 added price
LSc = (LSb_cost./SLS)

Bb_cost = (B_b*B_cost + B_l*CaCO3_cost).*B_pt;   %Sale cost
Bb_cost1 = (B_b*B_cost + B_l*CaCO3_cost).*B_CCE; %CaCO3 added price
Bc = (Bb_cost./SB)

CMax = max(horzcat(LAc, LSc, Bc));
LAcN = LAc./CMax;
LScN = LSc./CMax;
BcN = Bc./CMax;

b0=3; b1=4;
x = linspace(1,100); % Adapt n for resolution of graph
y = 142.5/0.8;

LAb_cost1 = (LA_b*LA_cost + LA_l*CaCO3_cost).*LA_CCE;%CaCO3 added price
LSb_cost1 = (LS_b*LS_cost + LS_l*CaCO3_cost).*LS_CCE;%CaCO3 added price
Bb_cost1 = (B_b*B_cost + B_l*CaCO3_cost).*B_CCE;     %CaCO3 added price

LA_b_gkg = [0.1 0.2 0.3 0.4 0.5].*10;       %g binder/kg pellets
LS_b_gkg = [0.72 0.9 1.08 1.26 1.44].*10;
B_b_gkg = [1 2 3 4 5 6 7].*10;

figure()
```

```
IndexLA = scatter(LA_b_gkg,LAb_cost1,60,'s','k',
'LineWidth', 0.6);
hold on
scatter(LA_b_gkg(3:5),LAb_cost1(3:5),60,'s','MarkerEdgeColor','k',
'LineWidth', 2);
hold on
IndexLS = scatter(LS_b_gkg,LSb_cost1,60,'^','k',
'LineWidth', 0.6);
hold on
IndexB = scatter(B_b_gkg,Bb_cost1,60,'o','k',
'LineWidth', 0.6);
hold on
scatter(B_b_gkg(7),Bb_cost1(7),60,'o','MarkerEdgeColor','k',
'LineWidth', 2);
hold on
CaCO3 = yline(y, 'k--')
ylim([175 200])
yticks([175 178 180:5:200])
set(gca,'XScale', 'log')
set(gca,'FontSize',12);
grid on
box on
ylabel('\$/ton CaCO$_3$ added', 'fontsize', t, 'fontweight', 'bold');
xlabel('Binder inclusion [g/kg agglomerates]', 'fontsize', t,
 'fontweight', 'bold');
legend([IndexLA ,IndexLS, IndexB, CaCO3],'Na-A','LS', 'B',
'1 ton CaCO$_3$','Location','northeast');

b0=3; b1=4;
x = linspace(1,100); % Adapt n for resolution of graph
y = 142.5;

LAb_cost2 = (LA_b*LA_cost + LA_l*CaCO3_cost).*LA_pt; % price
```

```
LSb_cost2 = (LS_b*LS_cost + LS_l*CaCO3_cost).*LS_pt; % price
Bb_cost2 = (B_b*B_cost + B_l*CaCO3_cost).*B_pt;      % price
LA_b_gkg = [0.1 0.2 0.3 0.4 0.5].*10;       %g binder/kg pellets
LS_b_gkg = [0.72 0.9 1.08 1.26 1.44].*10;
B_b_gkg = [1 2 3 4 5 6 7].*10;

figure()
IndexLA = scatter(LA_b_gkg,LAb_cost2,60,'s','k',
'LineWidth', 0.6);
hold on
scatter(LA_b_gkg(3:5),LAb_cost2(3:5),60,'s','MarkerEdgeColor','k',
'LineWidth', 2);
hold on
IndexLS = scatter(LS_b_gkg,LSb_cost2,60,'^','k','LineWidth', 0.6);
hold on
IndexB = scatter(B_b_gkg,Bb_cost2,60,'o','k','LineWidth', 0.6);
hold on
scatter(B_b_gkg(7),Bb_cost2(7),60,'o','MarkerEdgeColor','k',
'LineWidth', 2);
hold on
CaCO3 = yline(y, 'k--')
ylim([140 160])
yticks([140 142.5 145:5:160])
set(gca,'XScale', 'log')
set(gca,'FontSize',12);
grid on
box on
ylabel('\$/ton Agglomerates produced', 'fontsize', t,
 'fontweight', 'bold');
xlabel('Binder inclusion [g/kg agglomerates]', 'fontsize', t,
 'fontweight', 'bold');
%title('Payback in terms of butternuts peeled in first 3 years');
legend([IndexLA ,IndexLS, IndexB, CaCO3],'Na-A','LS', 'B', '0 g/kg binder',
```

Arduino Code for rainfall simulator (Extract)

```
#include <SD.h>
#include <SPI.h>
#include <MyRealTimeClock.h>

File myFile;

MyRealTimeClock myRTC(6,7,8);

int motorPin = 3;
String ON;
String OFF;
int timeon, timeon1, timeon2, timeon3, timeon4, timeon5, timeon6;
int total;
float rainspeed = 3.25; // ml per sec

void setup() {
Serial.begin(9600);

while (!Serial) {
; // wait for serial port to connect. Needed for native USB port only
}
Serial.print("Initialising SD card...");
if (!SD.begin(4)) {

Serial.println("Initialisation failed!");
while (1);
}
Serial.println("initialisation done!");
pinMode(motorPin, OUTPUT);

//myRTC.setDS1302Time(00, 10, 9, 2 , 24, 7, 2020);
```

```
}
void loop() {
myRTC.updateTime();
Serial.print(myRTC.dayofmonth);
Serial.print(": ");
Serial.print(myRTC.hours); // Element 5
Serial.print(": ");
Serial.print(myRTC.minutes); // Element 5
Serial.print(": ");
Serial.println(myRTC.seconds);

if(myRTC.dayofmonth==21 && myRTC.month==7 && myRTC.year==2020
&& myRTC.hours==10 && myRTC.minutes==40 && myRTC.seconds==00){
  //digitalWrite(ledPin, HIGH);
  timeon = 0;
  telltime("ON", timeon);
  digitalWrite(motorPin, HIGH);
  timeon1 = 32600;
  delay(timeon1);
  timeon2 = 32600;
  delay(timeon2);
  timeon3 = 32600;
  delay(timeon3);
  timeon4 = 32600;
  delay(timeon4);
  timeon5 = 23446; //initial 500ml
  delay(timeon5);
  digitalWrite(motorPin, LOW);
  total = timeon + timeon1 + timeon2 + timeon3 + timeon4+ timeon5;
  telltime("OFF", total);
  myRTC.updateTime();
}
```

continued...

```
if(myRTC.dayofmonth==22 && myRTC.month==8 && myRTC.year==2020
&& myRTC.hours==9 && myRTC.minutes==00 && myRTC.seconds==00){
  //digitalWrite(ledPin, HIGH);
  timeon = 0;
  telltime("ON", timeon);
  digitalWrite(motorPin, HIGH);
  timeon = 32600;
  delay(timeon);
  timeon1 = 32600;
  delay(timeon1);
  timeon2 = 14185;
  delay(timeon2);
  digitalWrite(motorPin, LOW);
  total = timeon + timeon1 + timeon2;
  telltime("OFF", total);
  myRTC.updateTime();
}
delay(1000);
}

void telltime(String ONOFF, float timer){
myFile = SD.open("SimRain2.txt", FILE_WRITE);
myRTC.updateTime();

myFile.print(myRTC.dayofmonth); // Element 1
myFile.print("/");
myFile.print(myRTC.month); // Element 2
myFile.print("/");
myFile.print(myRTC.year); // Element 3
myFile.print(" ");
myFile.print(myRTC.hours); // Element 4
```

```
myFile.print(":");
myFile.print(myRTC.minutes); // Element 5
myFile.print(":");
myFile.println(myRTC.seconds); // Element 6
myFile.println(ONOFF);

if(ONOFF == "OFF"){
  float rainfall = float(timer / 1000)*3.25; //ml rained
  myFile.print("It rained ");
  myFile.print(rainfall);
  myFile.println("mL on this day.");
  myFile.println("");
  myFile.close();
}else{
  myFile.close();
}}
```

Appendix D: Agglomerates

(a) Sodium alginate agglomerates

(b) Lignosulphonate agglomerates

(c) Bentonite agglomerates

Figure D.1: Agglomerates of different binders produced in the inclined disc agglomerator.

Appendix E: Rainfall data for May-July 2014-2017 in Malmesbury, South Africa

Table E.1: Daily rainfall from 1 May - 31 July 2014 - 2017, obtained from the South African Weather Services.

	Daily rainfall [mm]			
Date	2014	2015	2016	2017
1-3 May	0.0	0.0	0.0	0.0
4 May	3.8	0.0	0.0	0.0
5 May	0.0	1.0	0.0	0.2
6 May	0.0	0.0	0.0	0.0
7 May	0.0	0.0	1.2	0.0
8 May	12.6	0.0	0.0	0.0
9 May	2.2	0.0	0.0	0.0
10 May	1.0	0.0	0.0	4.8
11 May	0.0	0.0	0.0	0.2
12 May	0.0	0.0	2.2	0.0
13 May	0.0	5.8	0.2	0.0
14 May	0.0	0.2	0.0	0.0
15 May	6.8	1.6	0.0	0.0
16 May	0.0	0.2	0.0	0.0
17 May	0.0	0.0	0.0	0.0
18 May	0.0	0.8	3.6	0.0
19 May	0.0	0.0	0.2	0.0
20-22 May	0.0	0.0	0.0	0.0
23 May	0.4	0.0	3.0	0.0
24 May	0.8	0.0	0.0	0.4
25 May	0.0	0.8	0.0	3.0
26 May	0.0	0.4	0.0	1.8

Table E.1 (continued):

	Daily rainfall [mm]			
Date	2014	2015	2016	2017
27 May	4.0	0.0	0.0	0.2
28 May	10.6	0.0	0.0	0.0
29 May	7.0	6.0	0.0	0.0
30 May	0.2	4.8	0.0	0.0
31 May	5.6	0.2	0.0	0.0
1 Jun	2.0	3.2	0.0	0.0
2 Jun	5.0	16.8	0.0	0.0
3 Jun	10.0	8.6	0.0	6.0
4 Jun	15.4	0.0	0.0	0.0
5 Jun	5.2	0.0	0.0	0.0
6 Jun	0.0	0.0	0.0	11.8
7 Jun	0.0	0.0	0.0	10.8
8 Jun	7.8	0.0	0.0	1.0
9 Jun	7.0	0.0	21.8	0.0
10 Jun	0.0	0.2	0.2	17.8
11 Jun	0.0	0.0	0.0	0.2
12 Jun	0.0	0.0	0.0	0.4
13 Jun	0.0	0.0	4.0	1.2
14 Jun	19.6	0.0	10.0	1.0
15 Jun	6.8	10.6	5.0	0.0
16 Jun	0.0	4.0	0.0	2.2
17 Jun	0.0	0.0	0.0	0.0
18 Jun	11.4	0.0	0.4	0.0
19 Jun	0.0	0.0	26.2	3.6
20 Jun	0.0	0.0	0.6	0.0
21 Jun	0.0	0.0	0.0	8.6
22 Jun	0.0	0.0	0.0	1.0
23 Jun	0.0	20.6	0.0	0.0
24 Jun	0.0	8.4	0.0	0.0

Table E.1 (continued):

	Daily rainfall [mm]			
Date	2014	2015	2016	2017
25 Jun	8.2	0.0	0.0	0.0
26 Jun	4.4	0.0	7.0	0.0
27 Jun	0.0	0.8	2.2	4.4
28 Jun	0.0	0.0	0.0	0.2
29 Jun	0.0	0.2	0.0	0.0
30 Jun	0.0	0.0	9.4	1.6
1 Jul	0.0	0.0	1.6	0.0
2-3 Jul	0.0	0.0	0.0	0.0
4 Jul	21.0	0.0	0.0	0.0
5 Jul	4.2	0.0	10.8	0.0
6 Jul	0.4	0.0	0.2	0.0
7 Jul	0.0	0.0	0.0	0.0
8 Jul	0.0	0.2	0.0	3.8
9 Jul	0.0	0.0	0.0	6.0
10 Jul	0.0	0.0	0.0	0.0
11 Jul	0.0	7.8	0.0	0.0
12 Jul	0.2	0.4	0.0	0.0
13 Jul	0.4	0.0	0.0	0.0
14 Jul	0.0	0.0	5.2	0.2
15 Jul	0.0	0.2	2.8	11.6
16 Jul	0.4	3.2	0.0	0.0
17 Jul	16.8	20.4	0.0	0.0
18 Jul	6.8	0.0	0.0	0.0
19 Jul	0.0	0.0	3.2	0.0
20 Jul	0.0	0.0	17.0	0.8
21 Jul	0.0	0.0	1.6	0.0
22 Jul	0.0	13.4	4.8	0.0
23 Jul	0.0	8.6	0.2	0.0
24 Jul	17.0	0.0	0.0	0.4

Table E.1 (continued):

	Daily rainfall [mm]			
Date	2014	2015	2016	2017
25 Jul	12.8	0.0	0.0	5.8
26 Jul	17.2	0.0	10.2	0.0
27 Jul	0.2	0.0	4.2	0.0
28 Jul	0.0	0.0	13.4	0.0
29 Jul	0.0	16.8	0.0	0.0
30 Jul	0.0	8.2	0.2	0.0
31 Jul	0.0	0.0	0.0	0.0
TOTAL	255.2	174.4	172.6	111.0

Appendix F: Sample calculations

Calcium carbonate and calcium content from CaO

- XRF result for CaO (CaO_{XRF}) = 44.86% = 0.4486
- Molecular mass of Ca (M_{Ca}) = 40.078 g/mol
- Molecular mass of CaO ($\mathrm{M}_{\mathrm{CaO}}$) = 56.0774 g/mol
- Molecular mass of $CaCO_3$ ($\mathrm{M}_{\mathrm{CaCO_3}}$) = 100.0869 g/mol

$$\%_{\mathrm{CaCO_3}} = \mathrm{CaO}_{XRF} \cdot \frac{\mathrm{M}_{\mathrm{CaCO_3}}}{\mathrm{M}_{\mathrm{CaO}}}. \tag{4.1}$$

$$\mathrm{CaCO_3}\% = 44.86 \cdot \frac{100.0869}{56.0774}$$

$$= 80.06\%$$

$$\%_{Ca/Mg} = \mathrm{CaO}_{XRF} \cdot \frac{\mathrm{M}_{\mathrm{Ca}}}{\mathrm{M}_{\mathrm{CaO}}} \tag{4.2}$$

$$\mathrm{Ca}\% = 44.86 \cdot \frac{40.078}{56.0774}$$

$$= 32.06\%$$

Friability Loss

Example with 12.6 g/kg Lignosulphonate-limestone agglomerate:

- Initial mass (IM) = 6.5 g

- Final mass (FM) = 6.42 g

$$\begin{aligned} \text{Loss } [\%] &= \frac{\text{IM - FM}}{\text{IM}} \cdot 100\% \\ &= \frac{6.5 - 6.42}{6.5} \cdot 100\% \\ &= 1.23\% \end{aligned} \tag{4.3}$$

Normalised strength

- Average number of drops survived by agglomerates of 12.6 g/kg (R_a) = 3.13
- Maximum number of drops survived in the drop test (R_{max}) = 37

$$\begin{aligned} \text{NTI}_a &= \left(\frac{R_a}{R_{max}}\right) \\ \text{NTI}_{LS12.6} &= \left(\frac{3.13}{37}\right) \\ &= 0.083 \end{aligned} \tag{4.4}$$

Cost of per ton of agglomerates and $CaCO_3$

- Cost of limestone per gram ($\$_X$) = \$0.0001425/g
- Cost of lignosulphonate per gram ($\$_L$) = \$0.00043/g
- Grams of lignosulphonate at 12.6 g/kg per 1 ton of agglomerates ($X_{g/t}$) = 12600 g/t
- Grams of limestone for 1 ton of agglomerates ($L_{g/t}$) = 10^6 g/t
- Amount of $CaCO_3$ per limestone powder (x) = 0.8

$$\begin{aligned} \$/t \text{ agglomerates} &= (\mathrm{X}_{g/t} \cdot \$_X \ + \ \mathrm{L}_{g/t} \cdot \$_\mathrm{L}) \cdot \frac{10^6}{X_{g/t} + L_{g/t}} \\ &= (12600 \cdot 0.00043 \ + \ 10^6 \cdot 0.0001425) \cdot \frac{10^6}{12600 + 10^6} \\ &= \$146.08/t \end{aligned} \tag{4.5}$$

$$\begin{aligned} \$/t \ \mathrm{CaCO_3} \text{ applied} &= (\mathrm{X}_{g/t} \cdot \$_X \ + \ \mathrm{L}_{g/t} \cdot \$_\mathrm{L}) \cdot \frac{10^6}{x \cdot L_{g/t}} \\ &= (12600 \cdot 0.00043 \ + \ 10^6 \cdot 0.0001425) \cdot \frac{10^6}{0.8 \cdot 10^6} \\ &= \$184.90/t \end{aligned} \tag{4.6}$$

Soil lime requirement: Eksteen test

- Valence of Ca^{2+} = 2
- Valence of Mg^{2+} = 2
- Molecular weight of Ca^{2+} = 40.078 g/mol
- Molecular weight of Mg^{2+} = 24.305 g/mol
- ICP result for Ca^{2+} (R_{ICP}) = 16.797 mg/ℓ
- ICP result for Mg^{2+} (R_{ICP}) = 12.748 mg/ℓ
- Mass of soil used for soil solution = 10 g
- Volume of filtrate collected = 50 mℓ

$$\text{meq } M^{2+}/\ell = R_{ICP} \cdot \frac{\text{cation valence}}{\text{cation molecular weight}} \tag{4.7}$$

$$\text{meq } Ca^{2+}/\ell = 16.797 \cdot \frac{2}{40.078}$$

$$= 0.8382 \text{ meq}/\ell$$

$$\text{meq } Mg^{2+}/\ell = 12.748 \cdot \frac{2}{24.305}$$

$$= 1.049 \text{ meq}/\ell$$

$$(Ca + Mg) \text{ cmol.kg}^{-1} = \frac{1}{\text{Soil weight(g)}} \cdot \frac{\text{Extract volume(m}\ell)}{10} \cdot (\text{meq } Ca^{2+}/\ell + \text{meq } Mg^{2+}/\ell) \tag{4.8}$$

$$= \frac{1}{10} \cdot \frac{50}{10} \cdot (0.8382 + 1.049)$$

$$= 0.9436 \text{ cmol.kg}^{-1}$$

- Volume of NaOH required to complete titration ($\text{m}\ell_{\text{NaOH}}$) = 3.3 m$\ell$
- Molarity of NaOH solution ($[\text{NaOH}^+]$) = 0.1M
- Total volume of of soil solution collected ($\ell_{sol.}$) = 0.2 ℓ
- Mass of soil added to the soil solution (m_{soil}) = 0.02 kg

$$H \text{ [cmol.kg}^{-1}] = \frac{\text{m}\ell_{\text{NaOH}} \cdot [\text{NaOH}^+] \cdot \ell_{sol.}}{10 \cdot \text{m}_{soil}} \tag{4.9}$$

$$= \frac{3.3 \cdot 0.1 \cdot 0.2}{10 \cdot 0.02}$$

$$= 0.33 \text{ cmol.kg}^{-1}$$

- R-value = 10
- Titratable acidity (H) = 0.33 cmol.kg^{-1}
- Exchangeable calcium and magnesium ($Ca + Mg$) = 0.9436 cmol.kg^{-1}

$$\begin{aligned} LR\ [\text{t/ha CaCO}_3] &= \frac{4[R \cdot H] - (Ca + Mg)}{R + 1} \\ &= \frac{4[10 \cdot 0.33] - 0.9436}{10 + 1} \\ &= 1.114\ \text{t/ha} \end{aligned} \tag{4.10}$$

Effect of the agglomerates on a soil profile

- Calculated Eksteen lime requirement (LR) = 1.114 t/ha = 0.01114 g/cm^2
- Surface area of the soil column (A) = 283.52 cm^2
- Grams of lignosulphonate at 14.4 g/kg per 1 kilogram of agglomerates ($X_{g/t}$) = 14.4 g/kg
- Grams of limestone at 14.4 g/kg per 1 kilogram of agglomerates ($L_{g/t}$) = 1000 g/kg

$$\begin{aligned} \text{mass of agglomerates applied} &= \frac{LR \cdot A \cdot (X_{g/t} + L_{g/t})}{0.8 \cdot L_{g/t}} \\ &= \frac{0.01114 \cdot 283.52 \cdot (14.4 + 1000)}{0.8 \cdot 1000} \\ &= 4.00\ \text{g} \end{aligned} \tag{4.11}$$

Appendix G: Statistical equations obtained from the CCD results

Table G.1: The regression equation and R^2 values of each of the surface plots in Section 4.2 as determined through an ANOVA of the data obtained from the two CCDs described in the section.

Figure	Factor x	Factor y	Surface plot equation	R^2
5.1a	speed	water add.	-92.545721646361 + 2.1204781970832·x - 0.033229866403969·x^2 + 10.9153719029·y - 0.3027789244799·y^2 + 0.02066·x·y	0.86
5.1b	liquid add.	speed	40.993288824202 - 0.841494728638·x - 26.333439314479·x^2 - 4.363995148068·y - 0.51596659585207·y^2 - 0.4922534405·x·y	0.74
5.2	liquid add.	Na-A conc.	-83.266699873509 + 11.280592056234·x - 0.30876843145635·x^2 + 21.80435796689·y - 5.2926594721659·y^2 + 0.25825·x·y	0.87
5.3	liquid add.	LS conc.	-92.963195580639 + 7.9060014706404·x - 0.2091404769651·x^2 + 23.72701357045·y - 2.2015465464612·y^2 - 0.046015294323301·x·y	0.42
5.4	water add.	B conc.	-310.99011716054 + 19.28098002824·x - 0.31424105971095·x^2 + 91.530124770246·y^2 - 9.5448160467133·y^2 -1.02288846875·x·y	0.88

Appendix H: Raw data

Drop test

Table H.1: The raw data obtained from the drop tests after 15 samples from each agglomerate type were tested. The data obtained is the number of drops that each sample survived before breaking.

	Repeat number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Na-A 1	1	1	2	1	1	2	1	2	2	2	3	2	2	2	2
Na-A 2	3	4	4	4	3	4	5	2	4	4	4	5	10	5	8
Na-A 3	13	10	13	10	7	14	7	7	6	9	9	17	7	18	10
Na-A 4	22	22	14	35	6	20	42	18	41	31	14	36	47	22	15
Na-A 5	28	17	41	24	53	55	62	43	63	46	42	15	12	9	52
LS 7.2	2	1	1	1	1	1	2	1	1	1	2	3	2	2	3
LS 9	1	1	5	2	2	1	2	1	2	1	4	2	2	3	1
LS 10.8	1	2	1	1	1	2	2	2	2	2	2	2	3	3	3
LS 12.6	2	2	2	3	2	5	2	3	7	6	3	2	2	2	4
LS 14.4	3	4	3	2	3	2	2	1	2	4	7	3	7	5	5
B 10	1	1	1	1	1	1	1	1	1	1	1	1	2	1	1
B 20	2	3	2	2	2	1	2	1	1	2	1	1	1	1	1
B 30	1	2	2	2	2	1	1	1	1	1	2	1	2	1	3
B 40	2	2	3	2	3	3	3	6	4	5	4	3	5	4	2
B 50	2	1	2	3	3	3	5	4	3	4	7	9	8	8	5
B 60	6	5	5	8	7	6	7	6	8	7	6	7	5	5	8
B 70	13	8	4	15	16	14	15	14	16	12	13	11	16	17	14

Friability test

Table H.2: The data obtained through the friability test carried out on three sample groups per agglomerate types, where the data is represented as the mass percentage of loss after the test.

	Repeat number		
	1	2	3
Na-A 1	52.92	34.1	21.54
Na-A 2	9.24	6.77	3.85
Na-A 3	1.39	2.16	5.68
Na-A 4	1.23	1.23	1.38
Na-A 5	3.07	8.01	2.92
LS 7.2	15.25	53.46	2.61
LS 9	2.61	23.27	3.69
LS 10.8	3.08	6.15	4
LS 12.6	3.54	3.39	1.84
LS 14.4	11.25	0.15	2
B 10	70.96	86.46	85.21
B 20	18.98	41.45	45.23
B 30	28	24.96	14.48
B 40	3.84	5.68	4.31
B 50	3.22	1.85	1.54
B 60	2.30	1.98	2.15
B 70	1.69	1.72	1.59

Compression test

Table H.3: The raw data obtained from the compression tests, where 9 samples of each agglomerate type were tested for the maximum compressive force an agglomerate could withstand before breaking.

	Repeat number								
	1	2	3	4	5	6	7	8	9
Na-A 1	3.21	3.39	3.35	4.64	7.2	5.74	4.08	4.73	5.72
Na-A 2	9.84	7.46	6.68	7.18	8.24	6.87	7.4	15.26	7.88
Na-A 3	19.31	19.91	12.9	13.72	11.53	11.8	18.54	16.5	
Na-A 4	18.92	17.76	16.09	16.07	15.97	14.3	14.36	12.04	12.03
Na-A 5	9.44	15.03	18.57	6.9	15.05	22.37	9.67	12.02	10.76
LS 7.2	2.79	3.18	2.97	4.65	3.77	3.95	3.95	3.85	5.44
LS 9	3.97	3.65	4.69	3.83	3.68	3.46	5.03	5.51	3.6
LS 10.8	4.08	3.25	2.81	4.3	2.18	1.74	4	5.61	4.71
LS 12.6	5.42	3.96	4.49	7.10	6.19	7.13	5.60	5.61	4.71
LS 14.4	4.4	4.35	5.61	5	7.27	6.8	10.49	5.18	5.35
B 10	1.68	2.13	2.27	1.27	1.69	1.31	2.25	2.65	1.49
B 20	6.07	4.91	9.09	4.13	3.99	3.58	3.57	3.98	1.92
B 30	4.47	10.38	6.38	10.43	9.10	5.57	6.59	6.25	10.01
B 40	11.42	12.96	14.10	11.72	12.30	6.09	7.95	6.71	7.07
B 50	8.38	10.67	10.58	7.41	10.25	15.49	10.28	8.89	7.87
B 60	8.96	9.35	11.12	11.02	8.69	10.84	9.88	12.02	11.68
B 70	15.24	10.83	15.08	16.91	14.37	15.33	16.44	17.02	16.59

Moisture disintegration test

Table H.4: The raw data obtained from the moisture disintegration test, where 15 samples from each agglomerate type were timed to determine the number of seconds each agglomerate type could withstand before total disintegration when saturated with water.

	Repeat number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Na-A 1	10	13	15	23	43	14	22	53	60	80	11	15	19	21	50
Na-A 2	20	33	52	57	61	20	22	26	40	52	37	41	45	47	57
Na-A 3	54	115	131	168	200	65	69	83	95	167	75	112	124	132	168
Na-A 4	127	136	192	260	273	201	247	291	311	318	225	273	302	324	346
Na-A 5	199	280	336	365	430	201	228	243	266	272	93	123	191	257	319
LS 7.2	60	85	135	161	252	86	101	128	164	188	71	224	235	263	278
LS 9	98	169	210	243	281	91	133	149	158	278	155	182	190	242	306
LS 10.8	24	188	221	236	253	150	261	339	391	449	196	221	233	242	284
LS 12.6	113	147	192	212	308	185	203	251	290	494	131	144	210	245	260
LS 14.4	68	114	126	137	183	151	265	600	643	726	177	273	296	357	399
B 10	14	19	21	22	24	28	41	50	55	64	25	28	31	34	37
B 20	47	56	62	73	88	32	41	54	70	145	48	51	55	60	75
B 30	118	166	172	180	188	116	223	285	357	402	64	123	201	317	409
B 40	304	393	433	446	459	187	304	434	461	522	253	323	331	425	721
B 50	437	485	542	579	620	300	330	360	445	542	362	388	402	478	583
B 60	335	465	478	482	560	346	373	441	460	621	308	323	480	606	616
B 70	269	383	486	557	584	362	613	704	846	930	409	507	554	568	908

Appendix I: XRF results

Soil column attempt 1

Table I.1: The XRF results of the soil segments of 5, 10, 15, 20 and 25 cm deep into the soil profile. The segments were treated with no agglomerates in the control, sodium alginate of 4 g/kg and 5 g/kg (NaA4, NaA5), 14.4 g/kg lignosulphonate (LS144) and 40 g/kg or 70 g/kg bentonite (B40, B70).

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
C 0-5	11.96	0.51	5.48	2.10	0.63	0.03	0.83	0.19	59.34	0.78
C 5-10	11.85	0.50	5.54	2.06	0.58	0.03	0.80	0.21	58.72	0.77
C 10-15	11.68	0.45	5.52	2.03	0.56	0.03	0.81	0.19	59.36	0.76
C 15-20	11.75	0.49	4.99	2.05	0.55	0.03	0.81	0.2	60.45	0.77
C 20-25	11.67	0.47	5.16	2.01	0.57	0.02	0.81	0.2	60.80	0.77
NaA4 0-5	11.69	0.60	5.45	2.02	0.60	0.02	0.84	0.19	59.50	0.74
NaA4 5-10	11.70	0.48	5.18	2.03	0.59	0.03	0.81	0.20	59.50	0.75
NaA4 10-15	11.70	0.46	6.09	2.04	0.57	0.03	0.77	0.20	58.11	0.76
NaA4 15-20	11.87	0.45	5.90	2.05	0.59	0.02	0.82	0.20	59.21	0.77
NaA4 20-25	11.54	0.46	4.97	2.01	0.57	0.02	0.80	0.19	59.11	0.76
NaA5 0-5	11.74	0.61	5.17	2.07	0.62	0.03	0.85	0.20	58.81	0.78
NaA5 5-10	11.72	0.49	5.39	2.04	0.56	0.03	0.81	0.20	59.25	0.77
NaA5 10-15	11.83	0.49	5.67	2.05	0.57	0.02	0.80	0.20	59.44	0.77
NaA5 15-20	11.72	0.47	5.25	2.06	0.57	0.02	0.79	0.19	59.44	0.78
NaA5 20-25	12.00	0.47	5.48	2.08	0.58	0.02	0.82	0.20	59.49	0.77
LS144 0-5	11.75	0.57	5.46	2.06	0.61	0.02	0.84	0.20	58.29	0.76
LS144 5-10	11.87	0.48	5.49	2.06	0.57	0.03	0.79	0.20	59.02	0.76
LS144 10-15	11.52	0.50	5.10	2.01	0.56	0.03	0.80	0.20	59.93	0.76
LS144 15-20	11.73	0.44	5.88	2.06	0.58	0.03	0.81	0.19	59.80	0.76

Table I.1 (continued):

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
LS144 20-25	11.68	0.49	5.08	2.03	0.53	0.03	0.82	0.20	58.99	0.76
B40 0-5	11.56	0.57	5.93	2.03	0.60	0.02	0.80	0.19	59.56	0.74
B40 5-10	11.95	0.47	5.39	2.09	0.56	0.02	0.81	0.20	60.13	0.78
B40 10-15	11.62	0.51	4.99	2.03	0.57	0.03	0.79	0.20	59.43	0.76
B40 15-20	11.74	0.46	6.21	2.04	0.57	0.03	0.82	0.20	59.59	0.76
B40 20-25	11.70	0.46	5.13	2.04	0.58	0.02	0.82	0.19	58.58	0.75
B70 0-5	11.82	0.62	5.31	2.07	0.63	0.03	0.87	0.19	59.29	0.75
B70 5-10	11.62	0.51	5.16	2.02	0.57	0.03	0.81	0.20	59.89	0.76
B70 10-15	11.81	0.47	5.44	2.04	0.57	0.03	0.80	0.19	58.86	0.76
B70 15-20	11.72	0.47	5.28	2.05	0.55	0.02	0.81	0.20	59.75	0.76
B70 20-25	11.85	0.45	5.49	2.05	0.56	0.02	0.81	0.19	59.90	0.76

Soil column attempt 2

Table I.2: The XRF results of the soil segments of 2.5, 5, 10, 15, 20 and 25 cm deep into the soil profile. There were no agglomerates in the control, 4 g/kg, 5 g/kg sodium alginate (NaA4, NaA5), 14.4 g/kg lignosulphonate (LS144) and 40 g/kg, 70 g/kg bentonite (B40, B70).

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
C 0-2.5	11.04	0.45	5.81	2.02	0.57	0.03	0.77	0.20	59.11	0.76
C 2.5-5	11.91	0.52	5.34	2.02	0.57	0.03	0.78	0.20	58.52	0.76
C 5-10	11.63	0.50	5.03	1.99	0.59	0.03	0.80	0.20	59.31	0.75
C 10-15	11.03	0.47	6.54	2.00	0.57	0.02	0.73	0.19	59.05	0.75
C 15-20	11.07	0.47	5.64	2.01	0.58	0.03	0.78	0.19	60.26	0.75
C 20-25	11.29	0.48	5.72	2.06	0.59	0.03	0.78	0.20	59.47	0.76
NaA4 0-2.5	11.42	1.02	5.09	1.96	0.80	0.03	0.75	0.18	58.81	0.74
NaA4 2.5-5	11.52	0.51	5.21	1.99	0.57	0.03	0.78	0.20	57.70	0.74
NaA4 5-10	11.58	0.46	5.80	1.98	0.56	0.02	0.79	0.20	59.37	0.74
NaA4 10-15	11.65	0.47	5.17	2.00	0.58	0.02	0.80	0.19	59.79	0.76
NaA4 15-20	11.82	0.49	5.44	2.04	0.57	0.02	0.78	0.20	59.01	0.77
NaA4 20-25	11.77	0.48	5.84	2.01	0.58	0.03	0.78	0.20	58.67	0.75
NaA5 0-2.5	11.57	0.95	5.31	2.00	0.65	0.03	0.78	0.20	58.51	0.75
NaA5 2.5-5	12.01	0.44	5.99	2.05	0.60	0.02	0.78	0.20	59.97	0.76
NaA5 5-10	11.67	0.51	5.19	2.01	0.57	0.03	0.82	0.20	59.18	0.77
NaA5 10-15	11.73	0.49	4.97	2.02	0.55	0.03	0.80	0.20	59.35	0.76
NaA5 15-20	11.75	0.47	5.59	1.99	0.57	0.03	0.80	0.20	59.03	0.76
NaA5 20-25	11.79	0.44	6.37	2.00	0.58	0.03	0.78	0.19	59.56	0.76
LS144 0-2.5	11.72	0.82	5.31	2.00	0.64	0.03	0.77	0.20	58.83	0.75
LS144 2.5-5	11.59	0.54	5.10	1.98	0.57	0.03	0.80	0.20	59.11	0.76
LS144 5-10	11.13	0.48	5.61	2.03	0.59	0.02	0.86	0.19	59.73	0.75
LS144 10-15	11.06	0.47	5.43	2.03	0.58	0.03	0.78	0.19	60.09	0.75

Table I.2 (continued):

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
LS144 15-20	11.23	0.48	6.05	2.08	0.60	0.03	0.79	0.20	58.68	0.76
LS144 20-25	11.23	0.47	5.96	2.04	0.59	0.03	0.80	0.20	59.25	0.75
B40 0-2.5	11.53	0.71	4.88	1.99	0.61	0.03	0.77	0.20	58.66	0.75
B40 2.5-5	11.60	0.50	5.04	1.97	0.58	0.02	0.80	0.20	58.21	0.74
B40 5-10	11.04	0.46	6.38	2.04	0.57	0.03	0.77	0.19	58.09	0.76
B40 10-15	11.45	0.49	5.56	1.97	0.57	0.03	0.78	0.19	58.52	0.74
B40 15-20	11.78	0.49	5.74	2.03	0.58	0.03	0.80	0.20	58.24	0.76
B40 20-25	11.85	0.44	6.41	2.03	0.57	0.02	0.75	0.20	60.19	0.75
B70 0-2.5	11.59	0.75	4.91	2.01	0.64	0.03	0.80	0.20	58.99	0.75
B70 2.-5	11.70	0.53	5.43	2.00	0.58	0.02	0.80	0.20	58.84	0.76
B70 5-10	11.79	0.46	6.80	2.03	0.57	0.02	0.77	0.21	58.85	0.75
B70 10-15	12.03	0.47	5.69	2.06	0.60	0.03	0.77	0.19	59.03	0.77
B70 15-20	11.40	0.50	4.72	1.97	0.55	0.02	0.80	0.19	59.18	0.75
B70 20-25	11.49	0.47	5.26	2.00	0.57	0.03	0.77	0.21	58.62	0.74

Appendix J: Published article

PARTICULATE SCIENCE AND TECHNOLOGY
https://doi.org/10.1080/02726351.2020.1833387

Taylor & Francis
Taylor & Francis Group

The effect of sodium alginate, lignosulfonate and bentonite binders on agglomeration performance and mechanical strength of micro-fine agricultural lime pellets

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ABSTRACT

Agricultural lime (crushed limestone) is often applied to acidic soils as the release of carbonate ions neutralize acid forming compounds, such as those added during fertilizer addition. Agglomerated micro-fine limestone is an attractive alternative to powdered limestone, mitigating product losses as a result of windy conditions during application. This article examines the production of agglomerates using sodium alginate, lignosulfonate and bentonite binders for micro-fine $CaCO_3$ powder. Central composite design was used to determine the optimal (i) amount of liquid, (ii) concentration of binder added to maximize the yield of agglomerates of 2–5.6 mm in diameter. Thereafter, four mechanical strength tests were carried out on the agglomerates, where strength was compared dependent on the binder and concentration thereof. The results show that lignosulfonate agglomerates performed the worst of the three binders, whereas agglomerates of >3 g/kg sodium alginate and 70 g/kg bentonite were acceptable in strength. While sodium alginate is a more expensive binder per gram, its high strength at relatively low levels may recommend its use industrially, contingent on economic modeling. This article successfully demonstrated the varying mechanical strengths of various limestone binders, which may assist with the development of novel soil amendment products.

KEYWORDS

Agglomeration; sodium alginate; bentonite; lignosulfonate; limestone

1. Introduction

Soil is a key component in agriculture and it is of vital importance that it is able to support successful and effective crop growth, providing support, anchorage, a water reservoir and mineral nutrients (Coleman and Thomas 1967). The majority of arable land is classified as acidic, which may lead to hindered crop growth due to, amongst other concerns, an increased solubility of toxic metals (Jovanovic et al. 2017). Soil pH is influenced by both acid- and alkaline-forming ions, where the leaching of nitrates and the input of acidifying substances, such as NH_4^+-based fertilizers, is one of the leading causes of acidified soil (Tang and Rengel 2003).

A buffer against soil acidification can be achieved by balancing acidic ions in the soil with Ca^{2+} and CO_3^{2-} (Jovanovic et al. 2017), for instance from limestone. When calcium carbonate dissolves in water (Equation (1)), the carbonate ions bonds with two H^+ ions forming a very weak acid, carbonic acid. As seen in Equation (2), carbonic acid readily forms H_2O and CO_2 when out of equilibrium, reducing the soil acidity caused by free H^+ ions.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \quad (1)$$

$$HCO_3^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l) + CO_2(g) \quad (2)$$

Crushed limestone, referred to as agricultural lime, can be applied to soil in many different forms, including as a suspension in water, as a powder or in pellet form (Feeco International Organization and Feeco International Organization 2018). Pelleted limestone is when powdered limestone is used along with a binder to form a pellet or agglomerate. Agglomeration is the simple technique of pelleting, requiring no external pressure in the mass production of a spherical product. This results in a product with many advantages over powdered or suspended limestone, including the ability to allow for a relatively uniform field application as it can be applied with conventional fertilizer spreaders. Application as an agglomerate also allows for a reduction in the loss of product in windy conditions when compared to that of powdered limestone (Feeco International Organization and Feeco International Organization 2018).

It is important to note that fine limestone is generally used in the agglomerating process, with a problem being the disintegration of the agglomerates during transportation and handling, which can result in losses if the powdery material is dispersed by wind (Darcovich 2008). Although this should be considered, it is also important to consider that the agglomerated limestone should be able to break up through environmental conditions, such as rain (Jovanovic et al. 2017). This allows the fine limestone to move to and impact deeper

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regions of the soil profile as it moves with the rainwater filtering through the soil. The binder used in the formation of the agglomerates should therefore be relatively water soluble.

A finer limestone particle will solubilize more readily than that of a larger particle size. The fine limestone particles that do not solubilize in the water can become encased in the water droplets without significantly hindering the flow of the rainwater through the compacted soil particles; hence the use of micro-fine limestone powder.

Although lignosulfonate is the binder most commonly used in the formation of limestone and animal feed agglomerates for agriculture (Tabil, Sokhansanj, and Tyler 1997; Albert and Langford 1998; Mallarino and Haq 2017), sodium alginate and bentonite are also potential binders used in various industries. Sodium alginate is often used as a binder in the pharmaceutical and cosmetics industry, while bentonite is used competitively with lignosulfonate in the animal feed industry (Lesser 1950; Clem and Doehler 1961). Sodium alginate, lignosulfonate and bentonite are included separately at different concentrations as binders for the agglomerates.

Sodium alginate is a polysaccharide sourced from brown seaweed and is known for its ability to form a viscous gel (Rinu and Joseph 2018). The sodium alginate polymers form cross-linking bonds with divalent ions such as calcium (Lim et al. 2016). This means that when sodium alginate comes into contact with the Ca^{2+} ion in $CaCO_3$, the divalent Ca^{2+} ion replaces the monovalent sodium ion in the polymer, linking the polymers to one another. With this process, the sodium alginate solution is expected to form a gel as the polymers develop stronger bonds, keeping the agglomerate in tact (Russo, Malinconico, and Santagata 2007; Browning et al. 2021). The potential of forming a solid product makes sodium alginate a binder of interest for limestone agglomerates.

Lignosulfonate is a completely water-soluble amorphous powder that originates as a by-product of the paper making industry. Lignosulfonate is a surface-active substance, capable of being adsorbed on the solid particles of a variety of materials. The solution that forms is generally viscous and capable of cation substitution. The lignosulfonate binder, which is liquid at the moment of adsorption will reduce the surface tension of the adsorbent, $CaCO_3$ (Nedosvitii et al. 1994). As a result of the adsorption, the lignosulfonate layer between the limestone particles is thickened and hardened, assisting in the formation of an agglomerate. The specific properties that are associated with lignosulfonate are owed to the presence of some of the functional groups structure. The sulfo-groups are responsible for the soluble nature of lignosulfonate (Nedosvitii et al. 1994; Madad et al. 2011), allowing it to become tacky when exposed to moisture and be integrated into the formation of agglomerates (Boregaard LignoTech Institution 2013). The nontoxic powder is often used for its binding agent in the animal feed industry (Veverka and Hinkle 2001).

Bentonite is a very fine-grained material largely composed of the clay, montmorillonite. Montmorillonite has a negatively charged lattice that is balanced by positively charged cations, commonly calcium or sodium cations. The montmorillonite lattices adsorb water, prying the adjacent flakes apart, causing an overall increase in the volume of the clay. Bentonite that is mixed with relatively small amounts of water forms a mixture with adhesive properties, with the strength depending on the bentonite/water ratio (Clem and Doehler 1961; Hayati-Ashtiani 2013). According to Jovanovic et al. (2017), the highly viscous clay material has no known negative effects on soil properties. Dried pellets or agglomerates that include bentonite are known to be strong enough to be transportable in large quantities and can absorb water many times its own mass (Liu, Xie, and Qin 2017). This property means that smaller agglomerates can swell to cover a larger surface area when placed in a moist environment, such as soil.

In order to produce a product to assess which binder might be most suitable for industrial use, agglomeration methods, common to industry, are considered. Disk agglomeration is a method used to continuously and simultaneously shape agglomerates by rotation and allow for classification by centrifugal segregation (Cuq et al. 2013). The angular velocity of the disk has an impact on the agglomerate size, with faster rotation producing smaller agglomerates (Pandey, Lobo, and Kumar 2012). Pandey, Lobo, and Kumar (2012) also state that the amount of water that is added during the granulation process has a great impact on the formation of the agglomerates. The water addition should not be less or more than the critical amount as this will either leave excess dry materials, or agglomerates that are too large. This critical amount of water to add during production must be determined experimentally for each agglomeration mixture to produce agglomerates of 2–5.6 mm in diameter. This desired size is required to allow for the distribution of the agglomerates to the soil using standard agricultural spreading equipment. This study aims to optimize and compare the agglomerative properties of three binding agents (sodium alginate, lignosulfonate and bentonite) for the production of micro-fine agricultural lime ($CaCO_3$) agglomerates. The agglomerates are tested and compared for mechanical strength, more specifically, impact-, abrasive- and compressive-strength, as well as resistance to degradation in water. The strength is important as an industrially suitable agglomerate should be economically viable, but also strong enough to withstand the handling and transportation process prior to application. The comparisons laid out in this article will assist in the development of soil amendment products with industrially appropriate characteristics.

2. Materials and methodology

The agglomeration process was assessed with reference to the speed of disk rotation, liquid addition and binder concentration to allow for a maximized mass fraction of agglomerates of 2–5.6 mm in diameter. Batches of agglomerates with different concentrations of sodium alginate, lignosulfonate and bentonite—included separately—were produced. These agglomerates underwent strength tests in

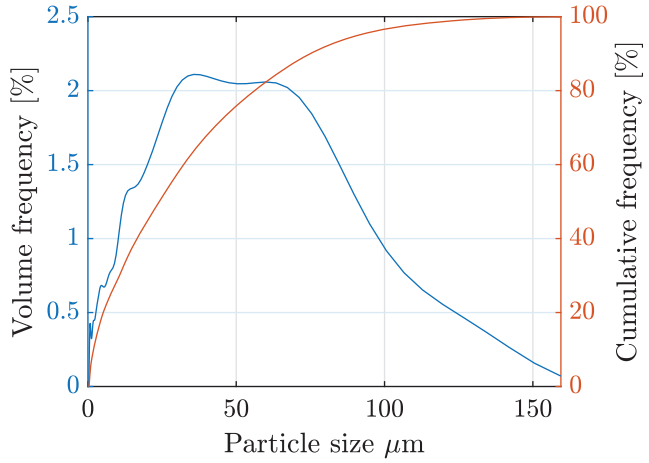

Figure 1. The volume frequency (blue) and the cumulative (red) particle size distribution for the agricultural lime used in this study. The curves represent the average of 3 replicates with error bars negligibly small.

Table 1. The chemical composition of the agricultural lime (Ag-lime) and powdered binders—sodium alginate (Na-A), lignosulfonate (LS) and bentonite (B)—as determined by XRF for selected major element analysis.

	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2
Ag-lime	0.61	44.86	1.58	0.07	8.15	0.26	0.05	0.02	4.82	0.12
Na-A	1.26	0.59	0.04	0.20	0.12	–	6.52	0.01	4.09	0.05
LS	0.01	0.01	–	0.87	–	–	11.15	0.07	0.39	0.01
B	14.60	1.12	2.88	0.80	3.15	0.05	2.25	0.03	58.05	0.20

Table 2. Central composite design showing the statistical points used to determine the optimum liquid addition and binder concentration for each of the binder types—sodium alginate (Na-A), lignosulfonate (LS) and bentonite (B).

	Statistical point				
	$-\sqrt{2}$	−1	0	1	$\sqrt{2}$
Na-A—binder [%/ml]	1.1	1.5	2.5	3.5	3.9
Na-A—liquid [ml]	6	10	20	30	34
LS—binder [%/ml]	2	3	5	7	8
LS—liquid [ml]	6	10	20	30	34
B—binder [%/100 g]	1	2	3	4	5
B—liquid [ml]	16	20	30	40	44

order to determine the role that a binder and concentration thereof has on the strength of an agglomerate.

All reagents used were of minimum reagent grade and purchased from Sigma-Aldrich unless otherwise stated. Lignosulfonate and was obtained as a by-product of the South African paper-pulping and bentonite (94% montmorillonite, 5.5% quartz, 0.5% mica) was obtained from Imerys Refractory Minerals. The sodium alginate that was used had a purity of 87.2 ± 0.2%. Micro-fine limestone powder, with the size distribution presented in Figure 1, was obtained from Equalizer AG with approximately 80% $CaCO_3$. Major element X-ray fluorescence (XRF) was used to determine the chemical composition of the limestone, sodium alginate, lignosulfonate and bentonite used in the production of the agglomerates, shown in Table 1. In order to maintain consistency, the water that was used in the production of the agglomerates went through reverse osmosis (RO). The resulting RO water had a conductivity of ≈3 µS/cm.

The disk agglomerator was designed in accordance with dimensions described by Capes (1980), where the disk had a diameter of 400 mm and rim height of 80 mm. The disk was made from polyvinyl chloride plastic (PVC), driven by a SEW R17 DT63K4 geared motor set to rotate at 37.5 rpm. A spray bottle was used to apply the liquid to the system during the agglomeration process. The inclination angle of the disk is set to 45°, in accordance with many literature sources (Capes 1980; Russo, Malinconico, and Santagata 2007; Cuq et al. 2013; Belwal et al. 2016). A manual screw conveyor was used in the agglomeration process to feed powder into the agglomerator system. The screw conveyor consisted of a funnel, a PVC screw with a 7 mm pitch placed inside a 15 cm PVC tube. The screw conveyor was set to feed the powder to the bottom right of the agglomerator disk as it rotated in the clockwise direction.

2.1. Agglomeration optimization

The optimization of the agglomeration process followed the central composite design (CCD) in Table 2 to specify the volume of liquid added to the system and the concentration of sodium alginate, lignosulfonate or bentonite in the respective agglomerate type. The CCD consisted of 2^2 factorial designs with a center point (0,0) and star points added, with a triplicate of the center point run. The mass fraction of the agglomerates of 2–5.6 mm diameter that were produced in a batch was chosen as the yield of the batch and formed the response variable for the analysis.

Sodium alginate and lignosulfonate were prepared as aqueous solutions in RO water under magnetic stirring for 30 min in capped bottles to avoid evaporation. The concentrations that the binders were added in are specified in the CCD. A bentonite-limestone powdered mixture was prepared at the concentration specified in Table 2. The mixture was shaken vigorously, resulting in a 100 g homogenized bentonite-limestone mixture. The amount of liquid that was added throughout the agglomeration process is specified in the table. For the liquid binders—sodium alginate and lignosulfonate—the liquid was the binder solution at the specified concentration. In the bentonite runs, the liquid that was added was RO water. These solutions were measured to the volume specified and added to a 50 ml spray bottle prior to each run.

The agglomeration processes that included sodium alginate and lignosulfonate made use of 100 g of limestone powder for each run, while the bentonite process made use of 100 g of the homogenized bentonite-limestone mixture with the bentonite concentration specified for that run. Thirty grams of this mixture was placed in the agglomerator disk and the remaining 70 g was placed in the funnel of the manual screw conveyor.

The motor was switched on, with each run being 30 min from when the motor reached its set speed of 37.5 rpm. The manual screw conveyor was turned to add additional powder to the constituents in the disk to continue agglomerate growth. The liquid was sprayed into the rotating disk throughout the run using the hand-held 50 m| spray bottle. A 150 × 50 × 2 mm metal sheet was used as a scraper to ensure that the materials did not stick to the base of the

disk. This was used throughout the run with care taken not to disturb the forming agglomerates, but rather to facilitate tumbling of the powder and smaller agglomerates as the disk rotates.

After each 30 min run the agglomerates were collected and dried at room temperature for 24 hours. These agglomerates were weighed to determine the total weight of the agglomerates produced in the run. Hereafter, the agglomerates were hand sieved with a 2000 µm- and 5600 µm-sieve. Those agglomerates that fell through the 5600 µm sieve and remained atop the 2000 µm sieve satisfied the 2–5.6 mm diameter size constraint set out for the product and were weighed, while those that did not were discarded. The weights of the well-sized agglomerates were used to determine the mass percentage of usable agglomerates, the response variable for the CCD.

A surface plot was generated for each of the binder types with the data obtained in the CCD in order to determine the optimum of the process variables in the production of agglomerates with a 2–5.6 mm diameter. These variables included the volume of liquid added to the system and the concentration of sodium alginate, lignosulfonate or bentonite in the respective agglomerate type.

2.2. Agglomerate strength

The agglomerates that were used in the strength tests in this section were produced using the same method discussed in Section 2.1.

The sodium alginate binder was prepared as a liquid having a concentration of 0.5%, 1%, 1.5%, 2% and 2.5% weight per volume RO water, where 20 ml of the solution was added to the system throughout each run. Eighteen milliliters of lignosulfonate solution was sprayed onto the unaltered limestone powder in the lignosulfonate-limestone agglomeration process. The solutions were prepared to have lignosulfonate concentrations of 4%, 5%, 6%, 7% and 8% per volume water. These binders used 100 g of micro-fine limestone in each run. Bentonite was added as a dry binder and was homogenized with the limestone powder to produce mixtures of 1:99, 2:98, 3:97, 4:96, 5:95, 6:94 or 7:93 bentonite to limestone powder, with a total mass of 100 g. Agglomerates that were produced with bentonite as a binder had 20 ml of RO water added to the system.

Each run was repeated in triplicate, resulting in three batches of like-agglomerates.

The fraction of agglomerates that were 2–5.6 mm in diameter—determined through sieving—were stored in a dry environment and the remaining agglomerates were discarded. These remaining, well-sized agglomerates underwent four different tests, namely the drop test, a friability test, a compression test and a moisture disintegration test.

2.2.1. Drop test

The drop test was adapted from Pietsch (2002) to assess the impact that each agglomerate type could typically withstand without shattering.

Fifteen agglomerates from each of the different binder types and concentrations were dropped onto a solid surface from a height of 1 m. The average of the number of drops that an agglomerate could survive while remaining completely intact was measured per binder concentration, giving an indication of the impact strength of the agglomerates in relation to the binder.

As there is not sufficient literature for limestone agglomerates that undergo this test, the agglomerates were compared to one another. Those agglomerates that remained intact for more drops than the average number of drops survived, were considered preferable over those that did not.

2.2.2. Friability test

The friability test was adapted from the pharmaceutical industry (World Health Organization 2012) and was used to compare the abrasive wear resistance of the agglomerates. The test makes use of a rotating hollowed cylinder with a 287 mm inner diameter and a 38 mm deep rim, placed at an angle of 10° with the vertical. A baffle with an 80.5 mm radius was fitted in the cylinder and the system was sealed with a lid.

Each test consisted of 6.5 ± 0.01 g of agglomerates sealed inside the cylinder that was set to rotate at 25 rpm for 100 rotations. The agglomerates were weighed prior to testing to obtain the initial weight (IW). After 100 rotations, the agglomerates were removed and hand sieved with a 2000 µm sieve to obtain the weight of agglomerates that continued to satisfy the size constraints, recorded as the final weight (FW). The average amount of abrasive loss experienced by each agglomerate type is obtained with Equation (3), showing the mass percentage of the agglomerates that turned to powder under abrasion.

$$\text{Loss} = \frac{IW - FW}{IW} \cdot 100\% \tag{3}$$

2.2.3. Compression test

The agglomerates were tested under an increasing compressive force using an MTS Criterion 44 Model C Universal Testing Machine. The machine was set to have a maximum load of 700 N, increasing at 0.5 mm/min. Testworks4 was used to record the increasing loads and breakage point of the sample. The compression test was carried out on 9–15 samples per binder type and concentration.

2.2.4. Moisture disintegration

The moisture disintegration time of the agglomerates was assessed by placing 15 agglomerates per binder concentration into a 500 ml beaker with 120 ml of RO water. The process was timed from when the agglomerates were placed in the water until the agglomerates had completely lost shape, as determined visually. The average time, in seconds, required for the agglomerates of a specific binder concentration to disintegrate was recorded as the result for this test.

The agglomerates were compared to one another in this test, where those agglomerates that maintained their shape

for longer than the average time were considered to be preferable over those that did not.

2.2.5. Total strength and desirability

Having the agglomerates undergo the strength tests, allowed the different agglomerate types to be compared on these measures and to evaluate their mechanical strength against each other. The comparisons between the agglomerates as well as strength data obtained in literature were combined to determine the suitability of the agglomerate type for use in industry. The results from each of the tests were summarized in a table to give an indication of how each of the agglomerate types fared in each test.

The agglomerate types were compared in terms of the resulting cost of the value product, $CaCO_3$ included in each agglomerate type. This was estimated as the cost of the product per percentage of the agglomerate that is $CaCO_3$, summarized in Equation (4). $X_{g/t}$ and $L_{g/t}$ represents the grams of binder and limestone included per ton of agglomerates, respectively. $\$_X$ and $\$_L$ representing the cost of the binder and limestone in \$/g, respectively.

$$\$/t\ \mathrm{CaCO_3}\ \text{applied} = (X_{g/t} \cdot \$_X\ +\ L_{g/t} \cdot \$_L) \cdot \frac{10^6}{L_{g/t}} \qquad (4)$$

The April 2020 cost of sodium alginate-, lignosulfonate- and bentonite-powder was estimated by Alibaba Group Organisation (2020a, 2020b, 2020c) to be \$2600/ton, \$430/ton and \$150/ton respectively. Micro-fine limestone was \$142.50/ton (Alibaba Group Organisation 2020d).

3. Results and discussion

The results in this section all contribute to the final goal of comparing the agglomerates from three different binding agents. This will give insight into the industrial viability of the binders—sodium alginate, lignosulfonate and bentonite—for the agglomeration of micro-fine limestone powder. Although, RO water was used in the production of the agglomerates, increased ionic activity in tap water (≈50 µS/cm) may have an impact on the formation and the strength of the agglomerates. This was however not quantified in this article, but the impact of the water on the properties of the agglomerates are expected to be minimal in comparison to that of the limestone and binder.

3.1. Agglomeration process

Disk agglomeration is a method used in industry to produce small (400 µm-20 mm) agglomerates (Feeco International Organization and Feeco International Organization 2018). The amount of water that is added during the granulation process has a great impact on the formation of the agglomerates. The moisture content should not be less or more than the critical amount as this will either leave excess powdered materials, or agglomerates that are too large (Pandey, Lobo, and Kumar 2012; Jacob et al. 2019). The size of the agglomerates was the major influencing factor on the usable yield of the production process. The amount of liquid that was added to increase the yield (those agglomerates of 2–5.6 mm in diameter) may differ with the different binders and is determined experimentally.

In order to determine the liquid requirement of the binders, it was required to determine if the binder concentration and the liquid requirement were independent of one another and the yield of correctly sized agglomerates.

Surface plots for each of the binders are corrected for the response variable of 0–100%, shown in Figures 2–4. The reasonable ranges used in the experimental design and the shape of the plots gave good approximations as to the information required, namely the significance of binder concentration and liquid addition, as well as the critical points required to maximize the yield.

With an ANOVA carried out on the data in each of the surface plots, it was determined that the volume of liquid that was added to the system was significant ($p < 0.05$), whereas the concentration of the binder was not ($p > 0.05$). Figure 2 shows that 100 g of limestone bonded by sodium alginate should have 20 ml binder solution, whereas only 18 ml lignosulfonate solution was critical for the yield of lignosulfonate-bonded agglomerates. Bentonite-limestone agglomerates required 22 ml of water for an increased yield. Each binder type therefore required approximately 20 ml of liquid for 100 g of powder to have a large yield of agglomerates. The significance of liquid addition is consistent with literature where Pandey, Lobo, and Kumar (2012) states that growth rates of the agglomerates is primarily dependent on the moisture added during the agglomeration process. If the moisture content was too little or too high, the corresponding growth rate will result in poorly-sized agglomerates after the 30 min period.

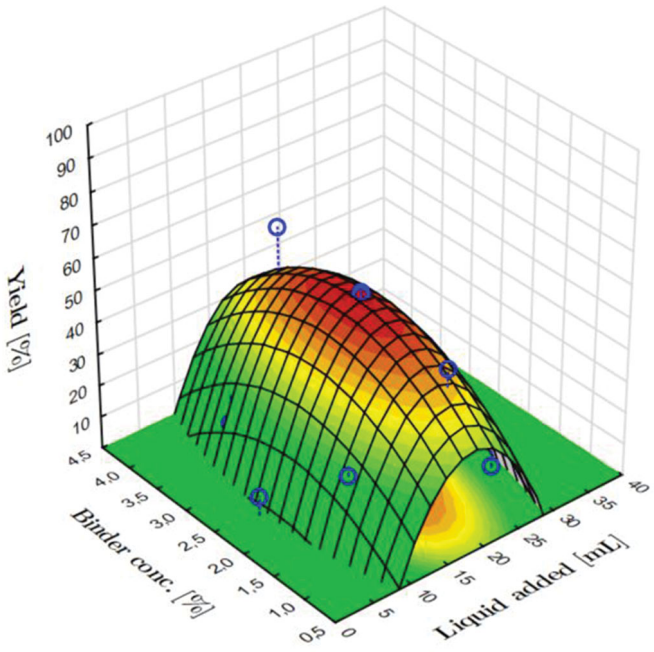

Figure 2. Surface plot for the yield response (corrected for yield > 0) to various concentrations of sodium alginate and volumes of binder solution added. Yield response is the percentage of agglomerates between 2 and 5.6 mm. At 20 ml liquid inclusion the estimated yield is 53.1% for 100 g limestone powder.

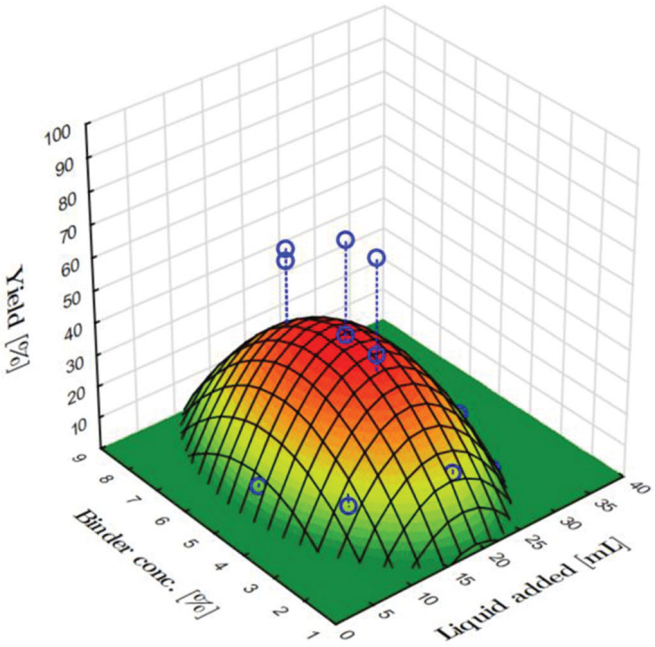

Figure 3. Surface plot corrected for the yield response (corrected for yield > 0) to various concentrations of lignosulfonate and volume of binder solution added. The high variability seen is owed to an increased yield (agglomerates of 2–5.6 mm diameter), at the additional points, 18 ml liquid addition at various concentrations, compared to that of the other volumes of liquid addition tested. The surface plot predicts a yield of 41% at 18 ml liquid addition.

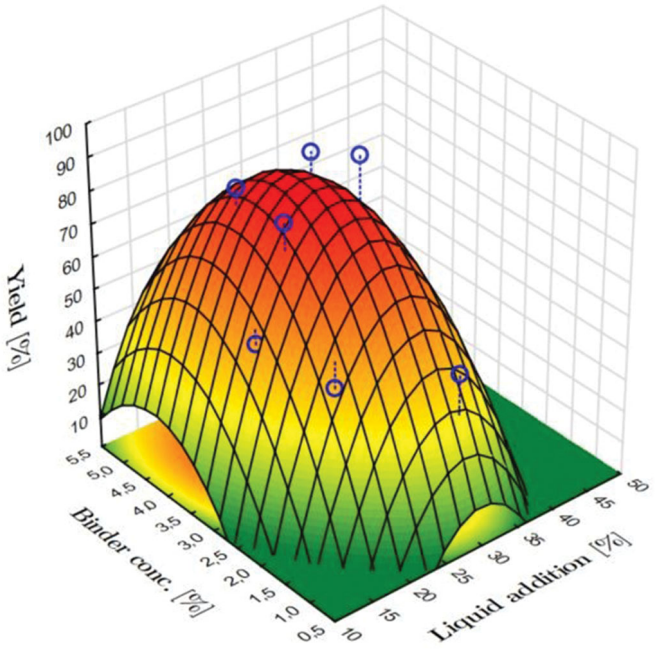

Figure 4. Surface plot for the yield response to various concentrations of bentonite and volumes of RO water added. Plot corrected for yields > 0.

The edges of the surface plot in Figure 2, show where too little or too much sodium alginate solution was added to the system. With a finite amount of powder in the system, an excess of sodium alginate solution caused the larger granules to attach to one another forming agglomerates that exceeded the upper size constraint. It was observed that when too little sodium alginate solution was added to the system, the calcium in the $CaCO_3$ powder reacted with the sodium alginate polymers available, forming a hardened outer layer of the granule that did not get re-coated with sodium alginate. The other powder granules could therefore not attach to these granules, resulting in many agglomerates that did not satisfy the lower size requirement and the yield was reduced. The resulting surface plot for sodium alginate is shown in Figure 2. At 20 ml liquid addition, the system is estimated to output a maximized yield of 53.1%.

Figure 3 shows the surface plot for lignosulfonate as a binder, where six additional runs with a liquid addition of 18 ml at various concentration were added to the system. Eighteen milliliters was chosen as an additional point because the CCD points in Table 2 showed very low yields and it was estimated to be a good intermediate liquid addition to potentially result in a higher yield. The predicted yield was maximized at 18 ml and was predicted to be 41%. The actual yields recorded at 18 m| were more than 30% higher than that of the yields recorded at other points, this caused a large amount of variation in the plotted response surface.

Figure 4 shows the CCD results from bentonite used as a binder. When too much water is added to the powdered mixture the excess water is absorbed by the bentonite increasing the surface area of each agglomerate during production. This causes more powdered limestone and bentonite granules to attach to the forming agglomerates, increasing the size further. When these agglomerates are dried, the increased size puts them out of the size limits, decreasing the yield of usable agglomerates. The maximized yield was estimated to be 90.3% at 22 ml water addition, which is much higher than that of the other binders tested. The response correction, altering the yield to 0–100%, distorts the influence that the binder concentration has on the yield (in the figure), an ANOVA on the results showed that binder concentration does not have a significant impact on the yield ($p < 0.05$).

The results obtained in this section allowed the adaptation of the agglomeration process in order to produce a maximized yield of agglomerates of 2–5.6 mm. The results were used in the further production of agglomerates to undergo strength tests using the different binder types and concentrations thereof.

3.2. Agglomerate strength

The strength of the agglomerates, as well as the disintegration of the agglomerates in water are important factors to consider when comparing the desirability of the agglomerates for industrial use. Agglomerates were produced using the different binders at various concentrations in order to assess the resulting strength of the agglomerates as a result of the binder.

The agglomerates were produced using the concentrations of binder, volume of water specified in Section 2.2, along with ≈100 g of micro-fine agricultural lime. Sodium alginate was included at 1 g/kg, 2 g/kg, 3 g/kg, 4 g/kg and 5 g/kg of dry material. Lignosulfonate was included at 7.2 g/kg, 9 g/kg, 10.8 g/kg, 12.6 g/kg and 14.4 g/kg dry material.

Bentonite was included in a larger volume with 10 g/kg, 20 g/kg, 30 g/kg, 40 g/kg, 50 g/kg, 60 g/kg and 70 g/kg dry material.

Drop-, abrasion resistance-, compression-, and moisture disintegration tests were used to assess the agglomerate strength of the produced agglomerates.

3.2.1. Drop test

The drop test assessed the resistance to breakage upon impact for each agglomerate type. The agglomerates typically experience impact stresses in the loading of silos or transportation vessels, as well as during packaging (Pietsch 2002). This test was therefore set up to have the agglomerates resist breakage on impact when dropped from an expected height in manufacturing, handling and transportation processes.

Fifteen agglomerates of each agglomerate type were dropped from 1 m, where the average number of drops survived by an agglomerate type was recorded as the result of the test.

The average number of drops survived by each agglomerate type is shown in Figure 5. The strong positive relationship between the binder concentration and the resistance to breaking on impact is clear. Sodium alginate-bonded agglomerates have a higher impact resistance to that of lignosulfonate and bentonite, even at a lower concentrations. This may be due to the ionic cross-linking between the calcium ion of the limestone and the sodium alginate polymers forming a very strong bond between the substances. This bond may be more resistant to breakage on impact compared to the lignosulfonate- and bentonite-bonded agglomerates that rely on adhesive properties due to adsorption (Clem and Doehler 1961; Nedosvitii et al. 1994; Russo, Malinconico, and Santagata 2007).

Figure 5 shows an increase in variability as the binder concentrations increase. This is a result of the error calculated as a function of the number of drops. The percentage variability is however relatively constant with all agglomerate types tested, even though the absolute variability is seen to have increased with binder concentration. As a stronger agglomerate is preferred, an agglomerate that remains intact for more drops is preferred. There is a lack of literature data for uncoated agglomerates of this size, therefore an absolute number of drops that an agglomerate should survive would need to be determined *in situ*. Regardless, these tests offer insight into at least the relative toughness of the different agglomerates. The binding strength of sodium alginate agglomerates, with regards to impact strength, had a larger increase with a very small increase in binder concentration in comparison to that of lignosulfonate and bentonite. Bentonite did however also have a significant increase in strength with each increase in binder concentration, but not as drastic as sodium alginate. An increase in the concentration of lignosulfonate had very little impact on the impact resistance, indicating that the lignosulfonate is not a strong binder at the concentrations tested. For the agglomerates tested in this article, the average number of drops survived was 7. Those agglomerates that could withstand more than the average 7 drops were considered to resist impact stresses well when the agglomerates were compared to one another.

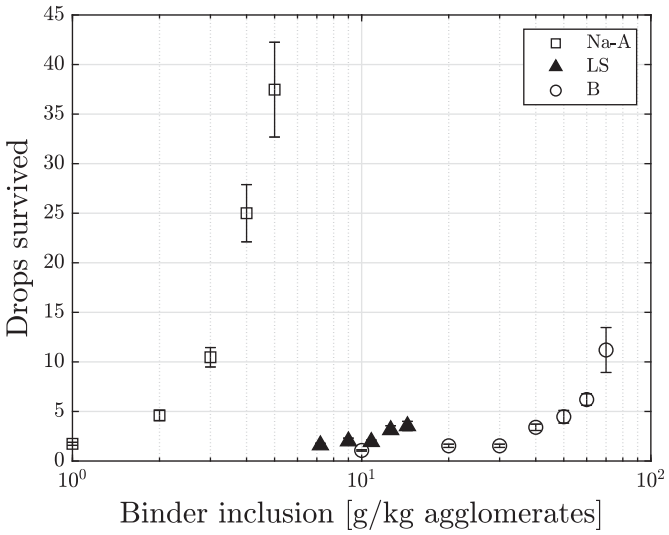

Figure 5. The average number of drops survived by agglomerates of different binder types, sodium alginate (▲), lignosulfonate (▲) and bentonite (°) when dropped from a height of 1 m in an impact strength test.

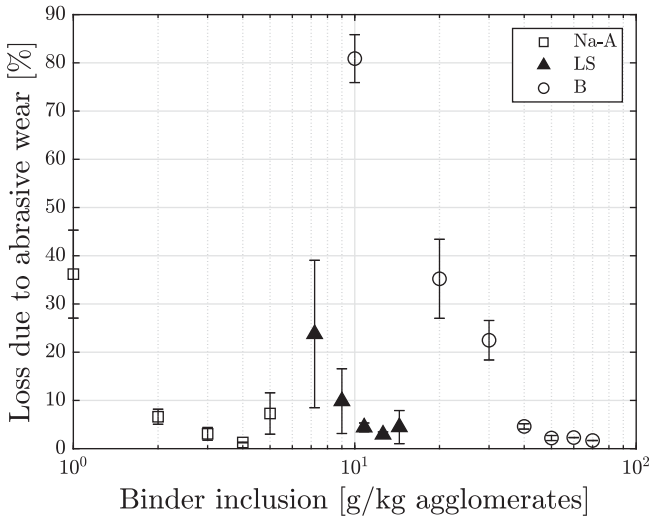

Figure 6. The mass percentage of loss experienced by agglomerates of different binders after 6.5 g of whole agglomerates were rotated in a cylinder at 25 rpm for 100 rotations. Symbols: □, sodium alginate; ▲, lignosulfonate; and °, bentonite.

3.2.2. Friability test

The results from the friability test give an indication of the wear an agglomerate may experience through abrasion, such as that of the agglomerates rubbing against one another once packaged or during transportation.

Figure 6 shows that there is a negative relationship between the concentration of binder in an agglomerate and the loss due to abrasion. The lower concentrations tested for each binder fare poorly, while at higher concentrations all the binders perform similarly in resisting abrasive wear. The slightly increased loss at 5 g/kg sodium alginate and 14.4 g/kg lignosulfonate may be due to crusts forming around the agglomerates at higher concentrations of binder, which is

sloughed off with the abrasion. The loss due to abrasion does, however, generally decrease with an increase in the binder concentration, alluding to the stronger bonds that were formed within the agglomerate due to the increase in binder.

Most fertilizers suffer a 0.4–21% degradation during mass abrasion resistance tests (Rutland 1986). This test is adapted from use on pharmaceutical tablets where the maximum allowable degradation is 1% (World Health Organization 2012). With these sources considered, agglomerates that exhibit a friability loss of <5% were considered to perform acceptably at resisting wear due to abrasive stresses. With this considered, agglomerates of (i) 3–5 g/kg sodium alginate, (ii) 9–14.4 g/kg lignosulfonate, and (iii) 40–70 g/kg bentonite were considered to fall within an acceptable range of loss due to abrasion.

3.2.3. Compression tests

During the compression of spherical agglomerates, the particle-particle bonds fail locally as flattening of the agglomerate occurs, forcing the particles into contiguous voids. As the particles shift into the voids, small dense regions form against the platens of the compression rig, causing the agglomerate to fail under tension along a circumferential crack joining the loaded poles (Pietsch 2002). Agglomerates that can withstand a large amount of compression will require more force for the dense regions to form and are therefore more resistant to cracking.

Figure 7 shows the results of the compression tests for each agglomerate of a binder type and concentration thereof. It is evident that there is a general increase in compressive strength with an increase in binder concentration.

As with the drop test, the sodium alginate-limestone agglomerates experienced a far higher compressive strength at far lower concentrations compared to that of the lignosulfonate- and most bentonite-limestone agglomerates. This could be due to the strong bond between the sodium alginate polymers and the calcium in the limestone. Bentonite of 70 g/kg inclusion does however result in limestone agglomerates that are competitive in compressive strength with the 3–5 g/kg sodium alginate-limestone agglomerates, but this does require far more dry binder. The crushing strength of some common fertilizers range from 7.8 to 40 N (United Nations Industrial Development Organization and International Fertilizer Development Organization 1998). Carlson and Le Capitaine (2020) states that the compressive strength of a fertilizer or a soil amendment product should be more than 17 N, whereas agglomerates of 2.36–2.80 mm should withstand a crushing force of 14.7 N (United Nations Industrial Development Organization and International Fertilizer Development Organization 1998). Limestone agglomerates of 5 g/kg sodium alginate proved to be in the range of 17 N. The sodium alginate- and bentonite-bonded agglomerates of 3–4 g/kg and 70 g/kg respectively did not resist a force as high as 17 N, but they are competitive with what is stated in literature in that they could withstand between approximately 13 and 16 N.

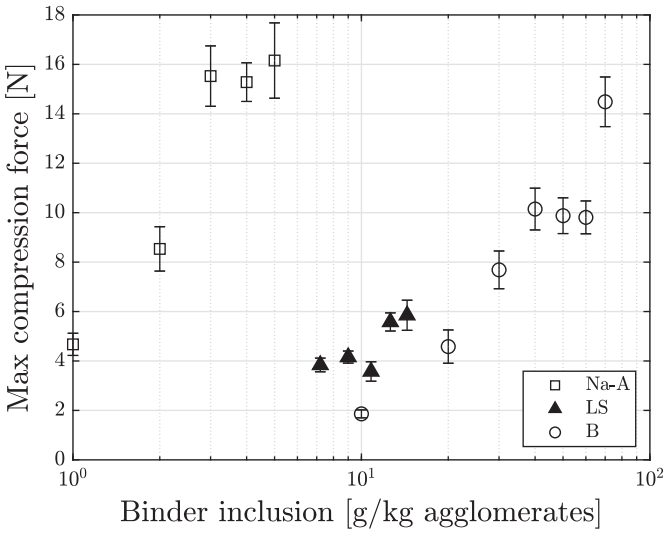

Figure 7. The maximum compressive force agglomerates of different binder types and concentrations can withstand when exposed to an compressive load increasing at 0.5 mm/min. Symbols: □, sodium alginate; ▲, lignosulfonate; and °, bentonite.

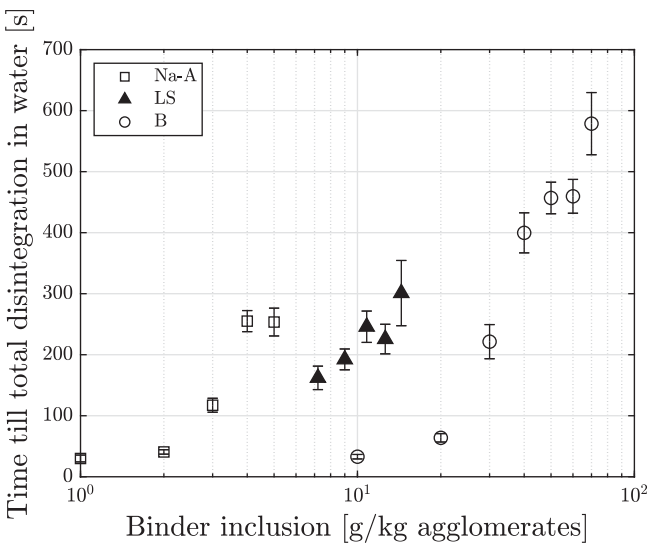

Figure 8. The average time it takes for agglomerates of different binder types, and concentrations thereof, to disintegrate when placed in 120 ml water. Symbols: □, sodium alginate; ▲, lignosulfonate; and °, bentonite.

3.2.4. Moisture disintegration

This test was developed as a method to compare the time taken for an agglomerate to completely disintegrate in water. This is an important factor to consider if the purpose of limestone is for it to penetrate further into the soil profile than where it is applied, so as to increase the pH of the soil at levels deeper than the surface, such as at the root zone of the crop. The agglomerates are expected to disintegrate, allowing the limestone to be transported through the soil profile with water from rain or irrigation systems. The agglomerates that resisted disintegration for longer during this test indicate that they will disintegrate when saturated by rain or irrigation water, rather than small amounts of moisture, e.g., during transportation and handling.

A graphical display of the time results showing the disintegration of the agglomerates is shown in Figure 8. It is clear

in the figure that the time required for the agglomerates to completely lose shape (disintegrate) when placed in water is dependent on the binder concentration.

The agglomerates exhibited different modes of disintegration, influenced by the bonding properties of the binders. Ionic cross-linking takes place between the sodium alginate polymers and the divalent calcium ion in the limestone powder (Russo, Malinconico, and Santagata 2007). This forms very strong bonding between limestone and sodium alginate, leading to flake-like disintegration of the agglomerates. The lignosulfonate-limestone agglomerates slowly lost shape when placed in water, owing to the water-soluble nature of the lignosulfonate. Bentonite can absorb water to up to 15 times its dry mass in water (Liu, Xie, and Qin 2017), allowing the agglomerates to swell when placed in the water. When the bentonite-limestone agglomerates became too large, they burst, giving the disintegrated agglomerate a larger surface area.

The sodium alginate agglomerates disintegrated slower than the other binders of the same binder concentration. The 4 g/kg- and the 5 g/kg-sodium alginate agglomerates did however perform similarly to that of the 10.8–14.4 g/kg lignosulfonate and 30 g/kg bentonite agglomerates. It is clear that the >40 g/kg bentonite agglomerates resist disintegration better than that of the other agglomerates tested. The swelling properties of the bentonite support this result as the agglomerates of increased bentonite inclusion will swell more prior to disintegrating, further postponing the disintegration of the agglomerate.

The agglomerates that resisted disintegration for the longest period of time give an indication that disintegration will take place over the course of the season rather than during the first rain, or worse, when exposed to moisture during handling. There is a lack of literature data for uncoated agglomerates of this size, therefore the time that an agglomerate should resist disintegration for would need to be determined *in situ*. Regardless, this test offers insight into the relative resistance to moisture degradation of the different agglomerates. For the agglomerates tested in this article, the average time before complete disintegration of a sample was 237 s. Those agglomerates that remained intact for the longest, but eventually disintegrated during this test were considered more desirable than those that disintegrated relatively quickly. In order to draw a comparison between the agglomerates tested, those that remained intact for >237 s were therefore considered preferable over those that did not.

3.2.5. Total strength and desirability

The total desirability of an agglomerate with a certain binder concentration was dependent on the impact strength, abrasive strength, compressive strength and resistance to moisture disintegration. Table 3 shows how each of the sodium alginate-, lignosulfonate- and bentonite—agglomerate types fare with regards to the different strength tests. The table confirms that there was a positive relationship between the concentration of a specific binder and the number of tests that the agglomerates satisfied.

As an agglomerate of a higher strength is preferred, an agglomerate that performed well in the tests was considered preferable and an agglomerate type that performed poorly in majority of the tests would not be strong enough to be considered for industrial use. The lignosulfonate- and bentonite-bonded agglomerates of 10.8–14.4 g/kg lignosulfonate or 30–60 g/kg bentonite, performed well in some tests, but were not strong enough to withstand compressive stresses associated with the processes prior to application, such as when agglomerates are stored in stockpiles. These agglomerates also performed poorly in comparison with the 3–5 g/kg sodium alginate- and 70 g/kg bentonite-bonded agglomerates in terms of impact strength and should therefore not be considered for industrial use. Calcium ions generally only bond weakly to lignosulfonate (Grierson, Knight, and Maharaj 2005), which could support the poor strength of all lignosulfonate-bonded limestone agglomerates at the concentrations tested.

The agglomerates of 4–5 g/kg sodium alginate and 70 g/kg were of industrial interest as they performed well in all aspects of strength tested. The 3 g/kg sodium alginate agglomerate type was considered to be of industrial interest as well. It performed well in terms of mechanical strength which is satisfactory if the agglomerates are protected from

Table 3. An indication of whether (+) or not (−) the binder types—sodium alginate (Na-A), lignosulfonate (LS) and bentonite (B)—at various concentrations satisfy the chosen criteria for each strength test.

Binder g/kg	Drop—< 7 ≤ +	Friability—> 5% ≥ +	Compression—< 14 N ≤ +	Disintegration—< 237s ≤ +	Tests satisfied
Na-A 1	−	−	−	−	0
Na-A 2	−	−	−	−	0
Na-A 3	+	+	+	−	**3**
Na-A 4	+	+	+	+	**4**
Na-A 5	+	+	+	+	**4**
LS 7.2	−	−	−	−	0
LS 9.0	−	+	−	−	1
LS 10.8	−	+	−	+	2
LS 12.6	−	+	−	+	2
LS 14.4	−	+	−	+	2
B 10	−	−	−	−	0
B 20	−	−	−	−	0
B 30	−	−	−	−	0
B 40	−	+	−	+	2
B 50	−	+	−	+	2
B 60	−	+	−	+	2
B 70	+	+	+	+	**4**

The bold numbers are associated with those agglomerates that satisfied a significant number of strength tests and were considered to be of industrial interest.

significant levels of moisture in processes prior to its application to the soil.

For an agglomerate to be worthwhile on commercial scale, it should be durable enough to withstand handling prior to application, as well as be affordable. The strength of an agglomerate could be compared to the other agglomerates types, but the cost of the binder should be justified by the strength that it provided. The cost of different binders and concentrations thereof impact the cost of the final product. Where a consumer will be attracted to a product of a lower cost and high strength, a product of too low a strength will likely break prior to application and is therefore not acceptable, regardless of the cost.

Figure 9 shows how the binder type and concentration thereof impacted the cost of the value product, $CaCO_3$, in the agglomerates. The agglomerate types marked as bold in the figures are those that were considered to be of industrial interest as per Table 3. Commercial farmers may be interested in the cost of the value product ($CaCO_3$) that is applied to the soil through application of the agglomerates, because scientific calculations are carried out on commercial farms to determine the amount of $CaCO_3$/ha that is required to increase soil pH to a specific value.

There is a positive relationship between the cost of the $CaCO_3$ that is applied through the application of the agglomerates and the concentration of binder in the agglomerate type. The stronger agglomerates or those that can be considered to be of industrial interest were the result of a higher cost of the value product. The value product, limestone, is included in high percentages (93.0–99.9%) in all agglomerate types, therefore the cost of the value product in the agglomerates was highly dependent on the cost of the limestone. This explains why the cost of $CaCO_3$ in each of the agglomerate types follow a similar trend in Figure 9. The benefit of a low concentration of sodium alginate is offset by its higher price, making lignosulfonate and bentonite competitive with it in cost, even at higher concentrations.

Agglomerates of 3–5 g/kg sodium alginate or 70 g/kg bentonite were the results of a 5.4–9.1% increase in the cost of the raw, un-agglomerated limestone powder. The benefit of avoiding waste due to the dispersion of limestone powder in windy conditions should far outweigh the added cost of binder used in the agglomeration of the limestone powder.

The additional strength that these agglomerates exhibit would result in a larger proportion of whole, undamaged agglomerates that can be applied to the soil, which would be in the best interest of the supplier as well as the user. This may be true for lignosulfonate agglomerates of a higher concentration if the trends seen in Figure 9 are followed.

It is also important to consider that an agglomerate type of 70 g/kg bentonite has a 93% concentration of limestone, whereas agglomerates of 3–5 g/kg sodium alginate are 99.5–99.7% limestone. The cost per ton of these bentonite agglomerates would be approximately $143, whereas these sodium alginate agglomerates cost $149–$155/ton of product. The bentonite-limestone product is, therefore, more cost effective in comparison to the sodium alginate-limestone product, when the agglomerates are considered rather than the cost of the limestone contained in the agglomerates.

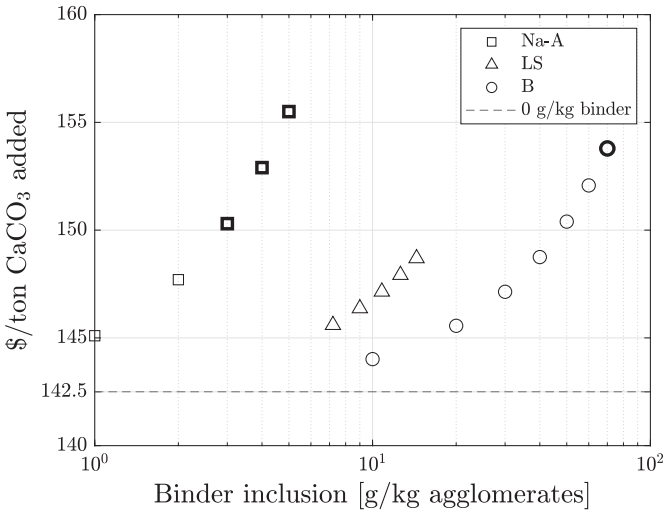

Figure 9. A graphical display of the cost of the value product, $CaCO_3$, as a results of the different concentrations of the different binders, sodium alginate (□), lignosulfonate (△) and bentonite (°) in the agglomerates. The bold markers represent those agglomerates that are of industrial interest and the dotted line indicates the April 2020 price of limestone powder, $142.50/ton (Alibaba Group Organisation 2020d).

4. Conclusions

Agricultural lime ($CaCO_3$) is typically applied to acidic soil in order to increase its pH to the crop-appropriate level, as well as avoiding the effect of acid solubilized toxic metals on root development. Agglomerates of micro-fine $CaCO_3$ can be applied to the soil rather than powdered limestone, as it is easier to handle in windy conditions. In this study, sodium alginate, lignosulfonate and bentonite are used as binders to ensure that the agglomerates remain intact after being produced in a bench-scale disk agglomerator. The agglomeration process was optimized with regards to the liquid required to produce a standard size agglomerate of 2–5.6 mm. The production of 100 g agglomerates required approximately 20 ml. After production, the agglomerates underwent an impact-, abrasion resistance-, compression- and moisture disintegration-tests to determine if they would be able to withstand the stresses of handling and transportation. Only agglomerates of 3–5 g/kg sodium alginate and 70 g/kg bentonite agglomerates performed satisfactorily in the strength tests. Exploitation of the stiff product that forms when sodium alginate comes into contact with calcium ions, proved valuable in the production of strong agglomerates that can be used in agriculture.

A purely component-based cost analysis of the different agglomerate types showed that the bentonite agglomerates were cheaper to produce than the sodium alginate and lignosulfonate agglomerates, while also exhibiting good strength. The cost of the value product, limestone, was however very similar in price for all agglomerates of similar strength, regardless of the binder type, where the stronger agglomerates added a materials cost of less than 10% to the powdered limestone.

The performance of the agglomerates in real-life simulations, such as in soil columns, could give a rounded view as to the applicability of the pelleted limestone on an industrial scale. This study examined the relative strength of binders on agricultural lime agglomerates. Strength was found to be strongly dependent on the concentration of the binder, with sodium alginate, or high concentrations of bentonite outperforming lignosulfonate as a binder in the production of strong agglomerates.

Acknowledgments

The authors would like to thank Gideon Schreuder from Equalizer AG and HP Steenkamp from Lime Chem for their contribution to this study.

Funding

AECI (Nulandis) assisted in funding with no involvement in study design; in the collection of data; analysis or interpretation of data; in the writing of the report; or in the decision to submit the article for publication.

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Appendix K: Permissions

The Alginate Demonstration: Polymers, Food Science, and Ion Exchange

Author: Louis H. Pignolet, Amy Sue Waldman, Linda Schechinger, et al
Publication: Journal of Chemical Education
Publisher: American Chemical Society
Date: Nov 1, 1998

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